Advances in Material Research and Technology

Meththika Vithanage
Giuseppe Lazzara
Anushka Upamali Rajapaksha *Editors*

Clay Composites

Environmental Applications

Springer

Advances in Material Research and Technology

Series Editor

Shadia Jamil Ikhmayies, Physics Department, Isra University, Amman, Jordan

This Series covers the advances and developments in a wide range of materials such as energy materials, optoelectronic materials, minerals, composites, alloys and compounds, polymers, green materials, semiconductors, polymers, glasses, nanomaterials, magnetic materials, superconducting materials, high temperature materials, environmental materials, Piezoelectric Materials, ceramics, and fibers.

Meththika Vithanage · Giuseppe Lazzara ·
Anushka Upamali Rajapaksha
Editors

Clay Composites

Environmental Applications

Springer

Editors
Meththika Vithanage
Ecosphere Resilience Research Center
Faculty of Applied Sciences
University of Sri Jayewardenepura
Nugegoda, Sri Lanka

Giuseppe Lazzara
Department of Physics and Chemistry
University of Palermo
Palermo, Italy

Anushka Upamali Rajapaksha
Ecosphere Resilience Research Center
Faculty of Applied Sciences
University of Sri Jayewardenepura
Nugegoda, Sri Lanka

Instrument Center
Faculty of Applied Sciences
University of Sri Jayewardenepura
Nugegoda, Sri Lanka

ISSN 2662-4761 ISSN 2662-477X (electronic)
Advances in Material Research and Technology
ISBN 978-981-99-2543-8 ISBN 978-981-99-2544-5 (eBook)
https://doi.org/10.1007/978-981-99-2544-5

© The Editor(s) (if applicable) and The Author(s), under exclusive license to Springer Nature Singapore Pte Ltd. 2023
This work is subject to copyright. All rights are solely and exclusively licensed by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors, and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Singapore Pte Ltd.
The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

Preface

This book focuses specifically on clay composites which has received recent attention for environmental applications such as water treatment. There is a growing interest in the scientific community in clay composites, whereas clays have been examined for environmental applications from long ago. Recent advances in characterizing composite materials led the pathway to conduct more research on clay composites, i.e., clay-biochar composites, etc. However, most focus has been centered in characterization of clay polymer composites or clay-nanoparticle composites, despite the real-world applications. Basic theories and fundamentals behind composite formation and its behavior in aqueous and solid systems will be discussed in detail for each of the clay composite. The chapters will be looking at the techno-economic performance of the clay composites described specifically for the future researchers to understand the pathway ahead. This book, with its varied parts listed above, is necessary for a number of reasons, including clay-biochar composites, Organoclay composites, clay polymer composites, environmental applications, and case studies.

Nugegoda, Sri Lanka	Meththika Vithanage
Palermo, Italy	Giuseppe Lazzara
Nugegoda, Sri Lanka	Anushka Upamali Rajapaksha

Acknowledgments

The editors would like to thank all the authors for their strong contributions. We would also like to appreciate and thank Priya Vyas, Senior Editor, Applied Sciences and Engineering, Springer Nature, for her inspiration as key input for this work. We wish to thank Mani Arasan Gandhi for the excellent coordination of this fascinating work. Last but not least, we are highly obliged to numerous colleagues for sharing knowledge, ideas, and assistance which helped in shaping this publication.

Contents

Overview (Introduction)

Clay-Biochar Composites

Organo-Clay Composites

Clay Polymer Composites

Environmental Applications

Editors and Contributors

About the Editors

Meththika Vithanage is a Professor and founder of the Ecosphere Resilience Research Centre, University of Sri Jayewardenepura, Sri Lanka. Before joining University of Sri Jayewardenepura, she has worked at the National Institute of Fundamental Studies, Kandy, and Adjunct Research Professor at the University of Southern Queensland, Australia. Her academic background covers environmental remediation of toxic metals, antibiotics, agrochemicals, serpentine soil chemistry, and waste biomass conversion. She received the prestigious Fayzah M. Al-Kharafi award from The World Academy of Science (TWAS) in 2020 and she became the Chairperson of the Young Scientists Forum in 2017. She received prestigious General Research Committee Award by the Sri Lanka Association for the Advancement of Science in 2019. She was awarded as the Best Young Scientist, 2018 by the Young Scientist Forum of the National Science and Technology Commission, Sri Lanka and in 2016 she became the Young Scientist in Chemistry by the National Science Foundation of Sri Lanka. She was selected as one of the Early Career Women Scientists by the Organization for Women Scientists in the Developing Countries, Italy. She served as the Chairperson of the Section for Engineering, Architecture and Surveying of the Sri Lanka Association for the Advancement of Science, Sri Lanka in 2018. She has received Presidential Awards for Scientific Publications for 10 years. Further, she was listed as Top 2% of the most cited scientists across various disciplines globally in 2017, 2019 and 2020. She has contributed over 150 Science Citation Indexed journal articles, over 30 book chapters and 4 co-edited books published by Elsevier Inc. She additionally contributed to 2 Korean patents and 1 Sri Lankan patent for environmental remediation of antibiotics using biochar and synthesis of nanozero valent iron. She has served in many national and international scientific committees to promote science.

Giuseppe Lazzara is full professor at the Department of Physics and Chemistry, University of Palermo, Italy. After his Ph.D. at the University of Palermo during which he was one year at Bayreuth University (Germany). He was post-doc at the Lund University (Sweden) carrying out research on supramolecular systems. He was the principal investigator of a project for young scientist (below 40 years old) entitled “Clay nanotubes for designing eco-compatible smart materials” founded by the Italian Minister of Research and University (FIRB 2012). His research is devoted to physical chemistry of nanostructured systems fuctional for the environment and cultural heritage. In particular the following main topics can be identified as bionanocomposites based on nanoclays as alternatives to conventional plastics, selective functionalization of nanoclay for smart applications and nanomaterials for conservation of cultural heritage. He contributed over 150 Science Citation Indexed journal articles, 1 co-edited book published by Elsevier Inc. and he is associate editor for Applied Clay Science journal. He has two patents on nanoclay based materials.

Dr. Anushka Upamali Rajapaksha is a Senior Lecturer, Faculty of Applied Sciences, University of Sri Jayewardenepura. She holds B.Sc. in Chemistry Special (Second upper) from the University of Peradeniya (2008), M.Phil (Chemical Sciences) from the University of Peradeniya (2012), and a Ph.D. in Biological Environment from Kangwon National University, South Korea (2015). Her research work includes the development of novel engineered/designer biochar as innovative solutions to environmental issues, mainly for remediating toxic heavy metals and pharmaceuticals contaminated soil and water, Heavy metal dissolution, Environmental remediation, etc. Dr. Rajapaksha has an excellent publication track record with over 60 SCI journal articles. She has received several awards and distinctions including the prestigious TWAS–Atta-ur-Rahman Award in Chemistry in the year 2022 by the UNESCO—World Academy of Sciences, Italy. President's Awards for Scientific Publications, Early Career Research Award (2021, Annual research award ceremony, University of Sri Jayewardenepura), Most Outstanding Young Researcher-(CVCD) Excellence Awards 2020 by The Committee of Vice-Chancellors and Directors. She is currently the Coordinating Editor of Environmental Geochemistry and Health (Springer) and Editorial Board Member for Journal of Hazardous Materials (Elsevier). Further, Dr. Rajapaksha is ranked among the top 2% of the world's best scientists in the 2020 list of outstanding researchers prepared by Elsevier BV, Stanford University, USA.

Contributors

Hansini Abeysinghe Department of Polymer Science, School of Polymer Science and Polymer Engineering, The University of Akron, Akron, OH, USA

N. M. Adassooriya Department of Chemical and Process Engineering, University of Peradeniya, Peradeniya, Sri Lanka

Jahangir Ahmad Soil Sciences Department, College of Food and Agricultural Sciences, King Saud University, Riyadh, Saudi Arabia

Memoona Ahmad School of Physical Sciences, University of the Punjab, Lahore, Pakistan

Munir Ahmad Soil Sciences Department, College of Food and Agricultural Sciences, King Saud University, Riyadh, Saudi Arabia;
Department of Soil, Water and Environment, Faculty of Agriculture, Food and Environment, Sana'a University, Sana'a, Yemen

Mutair A. Akanji Soil Sciences Department, College of Food & Agricultural Sciences, King Saud University, Riyadh, Saudi Arabia;
Department of Soil, Water and Environment, Faculty of Agriculture, Food and Environment, Sana'a University, Sana'a, Yemen

Abdullah S. F. Al-Farraj Soil Sciences Department, College of Food and Agricultural Sciences, King Saud University, Riyadh, Saudi Arabia;
Department of Soil, Water and Environment, Faculty of Agriculture, Food and Environment, Sana'a University, Sana'a, Yemen

Hamed A. Al-Swadi Soil Sciences Department, College of Food and Agricultural Sciences, King Saud University, Riyadh, Saudi Arabia;
Department of Soil, Water and Environment, Faculty of Agriculture, Food and Environment, Sana'a University, Sana'a, Yemen

Mohammad I. Al-Wabel Soil Sciences Department, College of Food and Agricultural Sciences, King Saud University, Riyadh, Saudi Arabia;
Department of Soil, Water and Environment, Faculty of Agriculture, Food and Environment, Sana'a University, Sana'a, Yemen

Yasmitha A. Alahakoon College of Chemical Sciences, Institute of Chemistry Ceylon, Rajagiriya, Sri Lanka

R. A. L. R. Amarasena National Institute of Fundamental Studies (NIFS), Hantana, Kandy, Sri Lanka

C. Arun Department of Biotechnology, Periyar Maniammal Institute of Science and Technology (Deemed to be University), Vallam, Thanjavur, Tamil Nadu, India

Ayse Dilek Atasoy Engineering Faculty, Environmental Engineering Department, Harran University, Şanliurfa, Turkey

W. M. A. T. Bandara Department of Chemistry, University of Peradeniya, Kandy, Sri Lanka

Irshad Bibi Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

Nanthi Bolan School of Agriculture and Environment, Institute of Agriculture, University of Western Australia, Perth, WA, Australia

Luiz Daniel da Silva Neto Drying Center of Pastes, Department of Chemical Engineering, Federal University of São Carlos (UFSCar), São Carlos, São Paulo, Brazil

Rohan S. Dassanayake Department of Biosystems Technology, Faculty of Technology, University of Sri Jayewardenepura, Pitipana, Homagama, Sri Lanka

S. M. Dassanayake Department of Decision Sciences, University of Moratuwa, Moratuwa, Sri Lanka

Hetvi Dave Faculty of Science, Department of Chemistry, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India

Cláudia Cseko Nolasco de Carvalho Department of Biology, State University of Alagoas, Santana Do Ipanema, Alagoas, Brazil

Lander de Jesus Alves State University of Santa Cruz (UESC), Ilhéus, Bahia, Brazil

Ícaro Mychel Gomes Leite de Sá Laboratory of Processes, Center of Technology, Federal University of Alagoas (UFAL), Maceió, Alagoas, Brazil

Pollyanna Vanessa dos Santos Lins Laboratory of Processes, Center of Technology, Federal University of Alagoas (UFAL), Maceió, Alagoas, Brazil

Joshua Nosa Edokpayi Water and Environmental Management Research Group, Faculty of Science, Engineering and Agriculture, University of Venda, Thohoyandou, South Africa

Randima Edussuriya Ecosphere Resilience Research Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, Nugegoda, Sri Lanka

Anusha Ekanayake Ecosphere Resilience Research Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka

Endene Emmanuel The World Bank, Washington, USA

Thusitha N. B. Etampawala Department of Polymer Science, Faculty of Applied Sciences, University of Sri Jayewardenepura, Nugegoda, Sri Lanka;
Center for Nanocomposite Research, Faculty of Applied Sciences, University of Sri Jayewardenepura, Nugegoda, Sri Lanka

Francesco Ferrante Dipartimento di Fisica e Chimica “Emilio Segrè”, Università degli Studi di Palermo, Palermo, Italy

José Teixeira Freire Drying Center of Pastes, Department of Chemical Engineering, Federal University of São Carlos (UFSCar), São Carlos, São Paulo, Brazil

Rafaela Gabriel Laboratory of Processes, Center of Technology, Federal University of Alagoas (UFAL), Maceió, Alagoas, Brazil

Sameera R. Gunatilake College of Chemical Sciences, Institute of Chemistry Ceylon, Rajagiriya, Sri Lanka

Sachira Hewawardhana Department of Biosystems Technology, Faculty of Technology, University of Sri Jayewardenepura, Pitipana, Homagama, Sri Lanka

Jiawei Huang Department of Materials Science and Engineering, College of Chemistry and Materials Science, Jinan University, Guangzhou, P.R. of China

Ming Huang Department of Materials Science and Engineering, College of Chemistry and Materials Science, Jinan University, Guangzhou, P.R. of China

Muhammad Mahroz Hussain Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

C. V. Ihalavithana Department of Chemical and Process Engineering, University of Peradeniya, Peradeniya, Sri Lanka

Muhammad Imran Centre for Inorganic Chemistry, School of Chemistry, University of the Punjab, Lahore, Pakistan

Shazia Iqbal Department of Soil Science, University of Sargodha, Sargodha, Pakistan

L. Jayarathna National Institute of Fundamental Studies (NIFS), Hantana, Kandy, Sri Lanka

C. L. Jayawardena Department of Earth Resources Engineering, University of Moratuwa, Moratuwa, Sri Lanka

S. Keerthanan Ecosphere Resilience Research Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, Nugegoda, Sri Lanka

Shoomaila Latif School of Physical Sciences, University of the Punjab, Lahore, Pakistan

Mingxian Liu Department of Materials Science and Engineering, College of Chemistry and Materials Science, Jinan University, Guangzhou, P.R. of China

Nahrir M. A. Lubis Soil Sciences Department, College of Food and Agricultural Sciences, King Saud University, Riyadh, Saudi Arabia;
Department of Soil, Water and Environment, Faculty of Agriculture, Food and Environment, Sana'a University, Sana'a, Yemen

Uthsara Malaweera Arachchi College of Chemical Sciences, Institute of Chemistry Ceylon, Rajagiriya, Sri Lanka

Danushika C. Manatunga Department of Biosystems Technology, Faculty of Technology, University of Sri Jayewardenepura, Pitipana, Homagama, Sri Lanka

Mukhethwa P. Mannzhi Water and Environmental Management Research Group, Faculty of Science, Engineering and Agriculture, University of Venda, Thohoyandou, South Africa

Marina Massaro Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF), Università degli Studi di Palermo, Palermo, Italy

Lucas Meili Laboratory of Processes, Center of Technology, Federal University of Alagoas (UFAL), Maceió, Alagoas, Brazil

R. T. Mohotti Department of Chemical and Process Engineering, University of Peradeniya, Peradeniya, Sri Lanka

Mohammed Awad Mousa Mousa Soil Sciences Department, College of Food and Agricultural Sciences, King Saud University, Riyadh, Saudi Arabia;
Department of Soil, Water and Environment, Faculty of Agriculture, Food and Environment, Sana'a University, Sana'a, Yemen

Muhammad Farrakh Nawaz Institute of Environmental Studies, University of Karachi, Karachi, Pakistan

Nabeel Khan Niazi Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan;
Faculty of Engineering and Science, Southern Cross University, Lismore, NSW, Australia

Fábio Carvalho Nunes Academic Department, Federal Institute Baiano (IF BAIANO), Bahia, Brazil

Pamoda Peduruhewa Department of Biosystems Technology, Faculty of Technology, University of Sri Jayewardenepura, Pitipana, Homagama, Sri Lanka

Dinusha Peramune Department of Biosystems Technology, Faculty of Technology, University of Sri Jayewardenepura, Pitipana, Homagama, Sri Lanka

M. D. R. Perera National Institute of Fundamental Studies (NIFS), Hantana, Kandy, Sri Lanka

Maheshika Perera National Institute of Fundamental Studies, Kandy, Sri Lanka

Udari Prasadini Perera Department of Chemical and Process Engineering, University of Moratuwa, Moratuwa, Sri Lanka

W. P. Yashodhara Perera Sri Lanka Institute of Nanotechnology, Nanotechnology and Science Park, Pitipana, Homagama, Sri Lanka

Majeti Narasimha Vara Prasad School of Life Sciences, University of Hyderabad, Hyderabad, India

Muhammad Imran Rafique Soil Sciences Department, College of Food and Agricultural Sciences, King Saud University, Riyadh, Saudi Arabia

Anushka Upamali Rajapaksha Ecosphere Resilience Research Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka;
Instrument Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka

Radhika Rao Faculty of Science, Department of Chemistry, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India

Hina Rasheed Department of Soil Science, Faculty of Agriculture and Environment, The Islamia University of Bahawalpur, Bahawalpur, Pakistan

Umair Riaz Department of Soil and Environmental Sciences, MNS University of Agriculture, Multan, Pakistan

Serena Riela Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF), Università degli Studi di Palermo, Palermo, Italy

Musiwa P. Sadiki Water and Environmental Management Research Group, Faculty of Science, Engineering and Agriculture, University of Venda, Thohoyandou, South Africa

H. H. P. B. Sandaruwan Department of Chemistry, Faculty of Science, University of Ruhuna, Matara, Sri Lanka

Rangabhashiyam Selvasembian Department of Environmental Science and Engineering, School of Engineering and Sciences, SRM University-AP, Amaravati, Andhra Pradesh, India

S. Seneweera University of Melbourne, Melbourne, Australia

A. Sethupathy Department of Chemical Engineering, Anjalai Ammal Mahalingam Engineering College, kovilvenni, Thiruvarur, Tamil Nadu, India

Muhammad Shahid Department of Environmental Sciences, COMSATS University Islamabad, Vehari Campus, Vehari, Pakistan

Muhammad Bilal Shakoor College of Earth and Environmental Sciences, University of the Punjab, Lahore, Pakistan

Muhammad Abubakar Siddique School of Physical Sciences, University of the Punjab, Lahore, Pakistan

Pelin Soyertaş Yapıcıoğlu Engineering Faculty, Environmental Engineering Department, Harran University, Şanlıurfa, Turkey

Padmaja Sudhakar Faculty of Science, Department of Chemistry, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India;
Faculty of Science, Department of Environmental Studies, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India

Nduvho M. Tshidumo Water and Environmental Management Research Group, Faculty of Science, Engineering and Agriculture, University of Venda, Thohoyandou, South Africa

Aisha Urooj School of Physical Sciences, University of the Punjab, Lahore, Pakistan

Muhammad Usama Soil Sciences Department, College of Food and Agricultural Sciences, King Saud University, Riyadh, Saudi Arabia;

Department of Soil, Water and Environment, Faculty of Agriculture, Food and Environment, Sana'a University, Sana'a, Yemen

Virang Vasveliya Faculty of Science, Department of Chemistry, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India

César Viseras-Iborra Department of Pharmacy and Pharmaceutical Technology, Faculty of Pharmacy, University of Granada, Granada, Spain;
Andalusian Institute of Earth Sciences, CSIC-UGR, Armilla, Granada, Spain

Meththika Vithanage Ecosphere Resilience Research Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka;
Sustainability Cluster, School of Engineering, University of Petroleum and Energy Studies, Dehradun, Uttarakhand, India;
Institute of Agriculture, University of Western Australia, Perth, Australia

R. Weerasooriya National Institute of Fundamental Studies (NIFS), Hantana, Kandy, Sri Lanka

Hasintha Wijesekara Department of Natural Resources, Sabaragamuwa University, Belihuloya, Sri Lanka

Madhuni Madhushika Wijesooriya Faculty of Graduate Studies, University of Ruhuna, Matara, Sri Lanka

D. M. D. Yakandawala Department of Botany, University of Peradeniya, Peradeniya, Sri Lanka

Mehmet İrfan Yeşilnacar Engineering Faculty, Environmental Engineering Department, Harran University, Şanlıurfa, Turkey

Fazila Younas Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

Amna Zulfqar Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

Overview (Introduction)

Clays and Clay Minerals: Long-Lasting Applications in Environmental Remediation

Madhuni Madhushika Wijesooriya, Hasintha Wijesekara, Nanthi Bolan, Anushka Upamali Rajapaksha, and Meththika Vithanage

Abstract Clay and clay minerals, either as adsorbents or immobilizing agents, exhibit a promising role in the elimination of contaminants from soil, water, and air. Therefore, this chapter aims to provide comprehensive knowledge of the capabilities of clay and clay-based composites for environmental remediation. Various physical and chemical modifications have been adopted to enhance the efficiency of the removal and/or adsorption processes of clay and clay-based composites. Bentonite/bentonite-based composites are the most frequently encountered clay type, followed by montmorillonite. Numerous parameters, such as pH, initial concentration of pollutants, their chemical nature, composite dosage, contact time, and temperature, affected the efficiency of the adsorption and elimination of pollutants. Depending on the type of pollutants and adsorbent composite used, the adsorption and elimination mechanisms of contaminants vary. However, the use of clay minerals and composites for the remediation of pollutants in soil has received less attention. Thus, this chapter provides new insights to broaden the application potential of clay/mineral composites in environmental remediation.

Keywords Adsorbents · Adsorption efficiency · Adsorption mechanisms · Bentonite · Clay-based composites

---

M. M. Wijesooriya
Faculty of Graduate Studies, University of Ruhuna, Matara 81000, Sri Lanka

H. Wijesekara (✉)
Department of Natural Resources, Sabaragamuwa University, Belihuloya 70140, Sri Lanka
e-mail: wijesekara@appsc.sab.ac.lk

N. Bolan
School of Agriculture and Environment, Institute of Agriculture, University of Western Australia, M079, Perth, WA 6009, Australia

A. U. Rajapaksha · M. Vithanage
Ecosphere Resilience Research Centre, University of Sri Jayewardanapura, Nugegoda 10250, Sri Lanka

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_1

1 Introduction

The contamination of soil, water, and air with pollutants of inorganic and organic origin has been accelerated due to anthropogenic activities [8]. These hazardous pollutants include pharmaceuticals and personal care products, poly- and perfluoroalkyl substances, pesticides, polycyclic aromatic hydrocarbons, dioxins, and organic and inorganic dyes [16, 38]. They cause serious negative effects on ecosystem functioning and adverse health effects in organisms, including humans [8, 61]. Several treatment approaches, such as membrane separation, ion exchange, coagulation, advanced oxidation, biological degradation, and photocatalytic degradation [8, 10, 17] have been employed to remediate soil and water contaminated with pollutants. Nevertheless, high implementation and maintenance cost, high energy consumption, and technical complexities have limited their application potential [40, 57]. Adsorption is a promising technique that can be employed to eliminate contaminants on a large scale in a sustainable manner [20, 24]. Therefore, a particular adsorbent should be inexpensive, compatible, efficient, recyclable, environment friendly, and suitable for large-scale application [43, 61, 80].

Over the past decades, clay and clay minerals, and their oxides (Al, Fe, and Si oxides), have deserved great attention in the remediation of contaminants as they are environmentally and economically feasible, highly abundant, and renewable [43, 55, 65]. Further, the physiochemical properties, such as high adsorption, ion exchange capacity, and high surface area, make clay minerals efficient adsorbents [43]. Therefore, as a natural scavenger of hazardous contaminants, clay can act as an adsorbent, an immobilizing agent, or a cleansing agent in soil and aquatic systems [55, 70]. However, in some instances, natural clay adsorbents have a limited potential to remediate pollutants from aqueous and soil media at large scales. Therefore, physical and chemical modifications with different functional groups (organic and inorganic agents) have been used as surface modifications to increase the selectivity, functionality, and effectiveness of natural clay minerals [57, 65]. Different types of clay and clay minerals have been employed depending on the purposes due to the variations in their structure, bonding mechanisms, particle size, cation exchange capacities (CEC), and layer charge. The extensively used clay minerals as adsorbents and immobilizing agents include bentonite, aluminium silicate, illite, kaolinite, montmorillonite (MMT), smectite, and zeolite [47, 57, 79, 82]. Apart from that, clay and clay mineral composites with synthetic polymers, biochar, and nanomaterials have enhanced their removal efficiencies due to their modified structure, adsorption capacity, high mechanical strength, and stability compared to the individual components [62, 76]. For instance, a recent review discussed that modified clays using different polymers can enhance the removal efficiency of pollutants [38]. Moreover, a recent review by Heidari et al. [34] revealed that photocatalysts (e.g., TiO_2, ZnO, CuxO, and Ag/Au) mediating clay composites have a high affinity to degrade and eliminate emergent micropollutants and inactivate harmful microbes in aquatic environments and wastewater effluents.

Pollutants can adsorb into clays or clay-containing composites can be due to either physisorption or chemisorption [28, 39, 67]. The pollutants interact with the surface of clays or clay composites to form chemical bonds such as hydrogen bonds, covalent bonds, coulombic attraction, van der Waals, π–π, anion–π, cation–π interactions, and hydrophobic interaction [26]. In some instances, a combination of these forces could act on the adsorption process [33]. Several parameters, including the structure and chemical properties of contaminants, the surface characteristics and functional groups of clay composites, and adsorption conditions such as pH, ionic strength, temperature, organic matter content, and trace element composition, affect the adsorption mechanism [6, 25]. These parameters are strongly interdependent with each other. Nevertheless, contradictory effects of these factors are reported depending on the type of contaminant and clay/composite used. Hence, an understanding of potential adsorption mechanisms and influencing factors is necessary for the selection and design of effective clay-based adsorbents to eliminate contaminants in the environment. Extensive research has been conducted in the last decade to investigate clay and mineral composites for the removal of contaminants in three environmental compartments: air, soil, and water. Therefore, this chapter aims to (i) discuss the recent research progress made on clay/mineral composites for the removal of contaminants, their adsorptive performance, and mechanism, (ii) identify the effect of several parameters on the adsorption capabilities of clay/mineral composites, and (iii) provide insights into the knowledge gaps and challenges of using clay-based material for the sustainable removal of contaminants.

2 Types and Characteristics of Clay and Clay Minerals as Remediating Agents

2.1 Naturally Occurring Clays and Clay Minerals

Clays are naturally occurring substances composed of fine-grained minerals that exhibit plasticity and occur in a layered structure (phyllosilicate) [52]. Tetrahedral silicates and octahedral hydroxide sheets are the building units of clay minerals. The 1:1 clay consists of one tetrahedral and an octahedral sheet (kaolinite and serpentine). In 2:1 clay, an octahedral sheet lies in between two tetrahedral sheets (illite, smectite, vermiculite, and montmorillonite), while in 2:1:1 clay mineral has a magnesium hydroxide sheet in the interlayer space between 2:1 sheet (chlorite) [42, 79]. In addition to the variations in their layered structures, clay minerals are categorized according to the types of substituted metals, the amounts and types of exchangeable ions found in the interlayers, the Si/Al ratio, and the impurities found in their structures [42, 56]. The findings of Shigidi et al. [68] revealed that the naturally occurring clay minerals, without any modifications, are also capable of removing pollutants (e.g., waste engine oil) with high efficiency. Further, Murtić et al. [53]

revealed that natural pyrophyllite and zeolite have the potential to reduce the trace element availability in soil.

2.2 Modified Clay Minerals and Clay-Based Composites

Depending on the nature of the contaminants, various treatment methods and modifications and combinations of techniques have been used to enhance the adsorption capabilities, reusability, and surface activities of clay minerals [54, 68]. These widely applied techniques include acid and alkaline treatments, thermal treatments, intercalation of functional groups such as organocations, biopolymers, and metal-pillared-clay minerals, and the combination of different clays/ clay minerals [68]. Modified oxide clays have been synthesized through the surface modification of oxides clays (Fe, Si, and Al oxides) [52]. Furthermore, natural clay minerals are chemically modified and functionalized by incorporating long alkyl chains, cationic surfactants, and magnesium phyllosilicate to produce organoclays and magnesium aminoclays [41, 52]. Apart from natural and synthetic polymers and surfactants such as polyamides, polyanilines, and ammonium surfactants, molecularly imprinted polymers (MIP) have also been used for the modifications [52, 74]. The high selectivity, stability, and adsorption efficiencies of MIP clays make them particularly useful for the separation of targeted contaminants from wastewater effluents containing multiple pollutants [74]. Acid-activated clay minerals increase the specific surface area and porosity due to the partial dissolution of cations [33]. Clay pillaring is another modification that is used to increase the interlayer space between clay layers and thus improve the adsorption process [54]. Thermal treatment methods improve clay mineral adsorption properties by removing impurities and hydroxyl ions, which improves stability [7]. Aside from single modification clays, recent studies by Chang et al. [15] and Barakan and Aghazadeh [12] developed multifunctional modified clays such as clay/ graphene oxide, porous clay heterostructure (PCH) that demonstrated high adsorption efficiencies against multiple contaminants.

Besides these modifications, numerous studies have investigated composites and nanocomposites that are made up of clay minerals and various polymers and biopolymers [6, 22, 35, 58]. These composites have shown improved properties such as high surface area, high compatibility and degradability, efficient adsorption capacity, and more active sites [59]. For instance, biochar-based clay composites have shown improved adsorption and immobilization of contaminants from soil and water due to the oxygen-containing functional groups [60, 69].

2.3 Characteristics of Clay Minerals

The properties of clay and clay minerals such as layered structures, regularly arranged silica-alumina framework, high specific surface area, cation exchange capacity, high surface electronegativity, and highly stable structure for catalyst recycling make them better suited for the remediation of pollutants in the environment. The commonly found cations in the exchange sites of clay minerals are Na^+, K^+, Mg^{2+}, and Ca^{2+} [42, 79]. The surface charge of clay minerals is produced as a result of the hydrolysis of Si–OH or Al–OH bonds in the lattice structure of clay. Depending on the silica structure and pH of the medium, the net surface charge of clay minerals varies either positively or negatively [42]. The easy separation methods following contaminant adsorption process is another advantage of using clay-based modification for remediation purposes [77].

3 Contaminants Removal and Their Mechanisms

As described in the above section, the application of clays and clay mineral composites for environmental remediation has received significant attention due to their high adsorptive performance and physiochemical characteristics. Numerous studies have developed different types of clay-based modifications and composites targeting many types of pollutants. Table 1 describes the adsorption performance of different types of clay and clay-based modifications and composites towards organic and inorganic contaminants in soil and water matrices.

The surface characteristics and the nature of the adsorbate have a direct effect on the adsorption mechanism. Figure 1 represents the most commonly identified adsorption mechanisms for clay/minerals/composites towards various contaminants.

3.1 Dyes

Certain types of dyes, especially organic dyes, are frequently used in the textile, paper, plastics, and automobile industries. A composite made from Fe_3O_4-bentonite/APTMA (magnetic 3-acrylamidopropyltrimethylammonium chloride intercalated bentonite) has exhibited high adsorption capacities of 2286 and 1210 mg/g for crystal violet and Congo red, respectively, due to the super-hydrophilic nature of the composite. The mechanism involved in the adsorption process is hydrogen bonding and electrostatic attraction between the adsorbent and dye molecules. Further, the study revealed that the efficiency of adsorption of the composite, Fe_3O_4-bentonite/APTMA, increased in the presence of trace metal ions. Thus, the composite is suitable for the removal of organic dyes of both anionic and cationic origin from industrial effluents [3]. The Fe_3O_4/kaolinite nanocomposite showed maximum adsorption capacities for methylene blue and Congo red under neutral pH conditions. The adsorption efficiency of the composite has been further increased by increasing the mass percentage of Fe_3O_4, with 7 mass% Fe_3O_4 exhibiting the best performance [29]. A study conducted by Ahmadi et al. [2] revealed that the MC/starch/$CoFe_2O_4$ nanocomposite (*montmorillonite* clay magnetically modified by starch and

Table 1 Natural and modified clay minerals, and clay composites for remediation of contaminants from soil and water

Contaminated medium	Clay and clay mineral	Modifier	Contaminant	Adsorption or removal capacity and remarks	Mechanism/s	References
Soil	Medical stone (Med) Montmorillonite (Mont)	Thiol (SH)-based material	Mercury and methylmercury (MeHg)	Reduction efficiencies of THg and MeHg from rice grains in Med-SH-amended were 78% and 81%, respectively, and in Mont-SH-amended were 67% and 78%, respectively Average reduction efficiencies of oxide-bound Hg in soil from Med-SH and Mont-SH amendments were 74% and 62%, respectively	Stabilize clay minerals on soil	[76]
	Nanoclays	Biochar formed from almond and walnut shell	Cd, Cu	Leaching of Cd content in soil has reduced effectively from 0.607 to 0.350 by composite of walnut biochar and nanoclay Cu content in soil has reduced effectively from 0.176 to 0.127 by composite of almond biochar and nanoclay	Surface complexation	[50]
Water	Montmorillonite	Quaternary ammonium	PFOA and PFOS	–	Electrostatic attractions	[63]

(continued)

Table 1 (continued)

Contaminated medium	Clay and clay mineral	Modifier	Contaminant	Adsorption or removal capacity and remarks	Mechanism/s	References
	Montmorillonite	HDTMA and poly-4-vinylpyridine-co-styrene mixture	PFOA	>90% defluorination	Catalysis through hydroxyl radicals as a result of the reaction between hydrated electron and oxygen	[18]
	Montmorillonite	Clay composite made from municipal solid waste biochar (MSW-MMT)	Tetracycline	78 mg/g	Physisorption (pore filling mechanism and intercalation) and chemisorption	[60]
	Bentonite	Composite magnetic 3-acrylamidopropyltrimethylammonium chloride intercalated bentonite (Fe_3O_4-bentonite/APTMA)	Cationic crystal violet and anionic Congo red dyes	Adsorption capacity of 2286 and 1210 mg/g for crystal violet and Congo red, respectively Adsorption capacity increased in the presence of trace metal ions Possesses high stability and regeneration potential	Hydrogen bonding and electrostatic interactions between adsorbent and dye molecules	[3]
	Bentonite	Polydopamine-modified Fe_3O_4-pillared bentonite	Crystal violet (CV) Rhodamine B (RB) Coomassie brilliant blue (BB)	Showed degradation efficiencies of 93% for CV and RB, and 99% for BB	Photo-Fenton reaction mechanism using H_2O_2 as oxidant	[4]
	Bentonite	Bentonite-modified biochar (*Alternanthera philoxeroides*) composite prepared by thermal treatment	Cd^{2+}	Adsorbed 36.9 mg/g and showed 81% adsorption efficiency compared to bentonite alone	Physisorption through ion exchange	[39]

(continued)

Table 1 (continued)

Contaminated medium	Clay and clay mineral	Modifier	Contaminant	Adsorption or removal capacity and remarks	Mechanism/s	References
	Commercial montmorillonite	Modified with Fe^{3+} polyhydroxy cations	Phosphate	Adsorption capacity of modified montmorillonite was 125–156% higher than that of the unmodified montmorillonite Presence of coexisting compounds (humic acid, fluvic acid, $NaNO_2$, $NaNO_3$, and NH_4Cl) did not affect the adsorption efficiency	Formation of inner-sphere complexes	[44]
	Bentonite	Activated by thermal treatment (TB)	Tetracycline	98.39% removal efficiency at pH 3 Optimum removal dosage 0.4 g/L with 95.05% removal efficiency Adsorption efficiency decreased with increasing electrolyte concentration	Three mechanisms; ion exchange by the intercalation of tetracycline into the interlayer space of TB, electrostatic interactions between negative binding sites in surface and cations of tetracycline, and complexation of tetracycline on the edge sites of TB	[47]
	Vermiculite	Abrupt heating at 1000 °C	Cr^{6+}	Removed 2.81 mol/g from aqueous solution	–	[49]
	Bentonite	Bentonite-modified biochar composite	Pb from wastewater effluents	99.20% removal efficiency	Electrostatic attraction between Pb and minerals	[62]

(continued)

Table 1 (continued)

Contaminated medium	Clay and clay mineral	Modifier	Contaminant	Adsorption or removal capacity and remarks	Mechanism/s	References
	Montmorillonite	Montmorillonite-modified biochar composite	Zn^{2+}	Adsorbed 241% more Zn^{2+} than simple biochar within 24 h	Electrostatic interaction between the negative charge of the interlayers and Zn^{2+}, ion exchange, and surface complexation	[69]
	Montmorillonite	Montmorillonite-modified biochar (wheat straw) composite	17β-estradiol (E2) (oestrogen contaminant)	Composite adsorbed 62.89 mg/g	π–π interactions and hydrogen bonding	[71]
	Na-bentonite	–	Cu^{2+}	~80% Na-bentonite modified with Al keggin cations decreased the adsorption	Exchange of Cu^{2+} and Na^{+} cations	[37]
	Montmorillonite	Nanocomposite composed of montmorillonite and a cationic surfactant (cetyltrimethylammonium bromide) with sodium alginate	Polycyclic aromatic Hydrocarbons (PAHs) (acenaphthene, fluorene, and phenanthrene)	Adsorbed acenaphthene, fluorine, and phenanthrene by 1.2, 0.9, and 2.5 mg/g, respectively	Hydrophobic interaction and van der Waals force	[20]
	Bentonite	Nanocomposite composed of nanobentonite-nanotitanium oxide chitosan	Levofloxacin and ceftriaxone	Removed 95% and 92.80% levofloxacin and ceftriaxone, respectively Removal efficiency increased with the increase in composite mass Removal efficiency of levofloxacin decreased in the presence of NaCl and $CaCl_2$	–	[48]

(continued)

Table 1 (continued)

Contaminated medium	Clay and clay mineral	Modifier	Contaminant	Adsorption or removal capacity and remarks	Mechanism/s	References
	Montmorillonite	Nanocomposite of montmorillonite/graphene oxide/$CoFe_2O_4$	Methyl violet	Adsorption capacity was 97.26 mg/g High recyclability and efficiency decreased with increasing the number of recycling steps	Electrostatic interaction between dye and the composite	[31]
	Bentonite	Modified with Arquad® 2HT-75 (IBA) and palmitic acid	Perfluorooctane sulfonate (PFOS) and phenanthrene (PHE)	Completely removed PFOS and PHE and 86.6% of Cu^{2+}	Cu^{2+} served as a bridge between the clay surface and organic contaminant to increase the adsorption efficiency of PFOS and PHE	[41]
	Clay	Cellulose (clay-cellulose biocomposite)	Pb^{2+}, Cd^{2+}	Adsorption capacities for Pb^{2+} and Cd^{2+} were 389.78 and 115.96 mg/g, respectively	–	[1]
	Kaolinite	Nanocomposite made from Fe_3O_4/kaolinite	Methylene blue and Congo red	Maximum adsorption capacities at 7 mass% Fe_3O_4 were 42.3 and 138.5 mg/g for methylene blue and Congo red, respectively	–	[29]
	Bentonite	Nanocomposite of Fe_2O_3/bentonite modified by doped TiO_2	Bisphenol A	Maximum adsorption capacity of 77.36 mg/g under neutral conditions Excellent reusability	–	[14]

(continued)

Table 1 (continued)

Contaminated medium	Clay and clay mineral	Modifier	Contaminant	Adsorption or removal capacity and remarks	Mechanism/s	References
	Bentonite	Bentonite-Fe/Pd	Tetracycline	Removed 97% tetracycline (20 mg/L) with less sorbent dosage (300 mg/L)	A redox reaction between the composite and tetracycline (TC) occurred to degrade organic molecules into simple biomolecules Degraded TC adsorbed into bentonite by intercalation between the interlayer	[32]
	Iranian bentonite	Arquad® 2HT-75 (IBA) IBA modified with palmitic acid (IBAP)	PFOS	IBA - 99.9 mg/g IBAP - 78.1 mg/g	IBA - Hydrophobic interaction and electrostatic attraction IBAP - Hydrophobic interaction	[41]
	Bentonite	Acidified using nitric acid	Fe^{2+}, Ni^{2+}, Zn^{2+} from pharmaceutical effluents	Removal efficiencies of Zn^{2+}, Fe^{2+}, and Ni^{2+} were 88.90, 81.80, and 75.50% at pH 8 Acid treatment increased active sites, porosity, and surface area for adsorption	Ionic and electrostatic interactions form several adsorption layers	[36]

(continued)

Table 1 (continued)

Contaminated medium	Clay and clay mineral	Modifier	Contaminant	Adsorption or removal capacity and remarks	Mechanism/s	References
	Montmorillonite	Magnetically modified by starch and cobalt-ferrite ($CoFe_2O_4$)	Methyl violet and methyl blue dyes Textile wastewater	98.67%, 99.45%, and 70% removal efficiencies for methyl blue, methyl violet, and textile wastewater, respectively	–	[2]
	Bentonite	Magnetically modified with $MnFe_2O_4$	Methylene blue	71.6% decolorization of methylene blue dye under dark conditions and decolorization efficiency increased under light illumination Composite showed antibacterial properties against *Staphylococcus aureus*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, and *Escherichia coli* at 100 µg/mL	Under light illumination photo-Fenton mechanism	[5]

(continued)

Table 1 (continued)

Contaminated medium	Clay and clay mineral	Modifier	Contaminant	Adsorption or removal capacity and remarks	Mechanism/s	References
	Bentonite	Nanocomposite formed from iron oxide/bentonite (Fe_3O_4/Bt. NC)	4-nitrophenol	99.5% at pH 11	Electrostatic interaction via Fe–O and Si–O and formation of new chemical bonds	[26]
	Bentonite	Magnetite bentonite-based adsorbents combined with reduced graphene (Fe_3O_4/Bent/rGO) and multiwall carbon nanotube (Fe_3O_4/Bent/MWCNTs)	Diesel oil	Maximum oil adsorption capacities of Fe_3O_4/Bent/rGO and Fe_3O_4/Bent/MWCNTs were 81.65 mg/g and 77.12 mg/g, respectively	Chemical, hydrophobic, π-π, and electrostatics interactions	[27]
	Kaolin	Chitosan-kaolin composite cross-linked with epichlorohydrin and tripolyphosphate	Auramine O (AO) dye	Maximum adsorption potential, 500 mg/L showed at pH 7.5 at 25 °C	Physical adsorption process	[67]

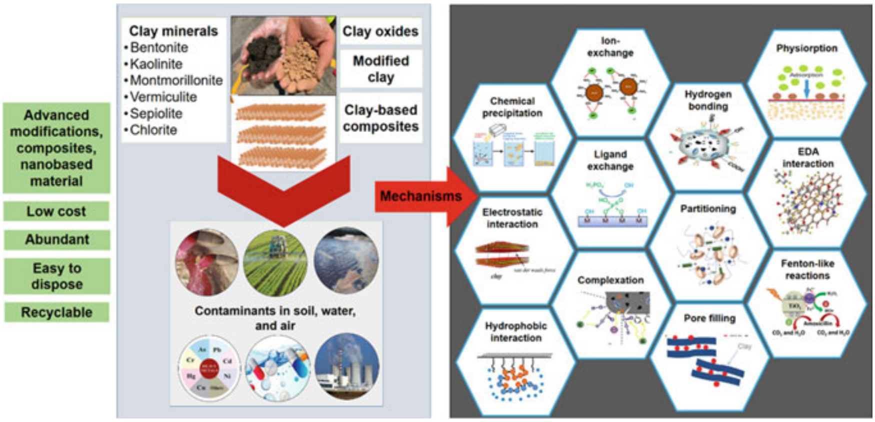


Fig. 1 Adsorption mechanisms of clay minerals/composites against contaminants in soil, water, and air

cobalt-ferrite) was capable of removing methyl violet, methylene blue, and textile dyes with efficiencies of 99.45%, 98.67%, and 70%, respectively. Another nanocomposite synthesized from bentonite clay with manganese ferrite ($MnFe_2O_4$) was capable of 71.6% decolorization of methylene blue under dark conditions. However, the efficiency of the decolorization process was enhanced under light illumination and destroyed methylene blue within eight minutes via a photo-Fenton mechanism [5]. Then polydopamine-modified Fe_3O_4-pillared bentonite composite showed both adsorptive and photocatalytic degradation against dyes in wastewater effluents. It degraded crystal violet and rhodamine B with 93% efficiency and Coomassie brilliant blue with 99% efficiency [4].

A chitosan-montmorillonite composite was also capable of removing methylene blue from wastewater effluents very rapidly with an eight minute contact time. Its recyclability, however, was limited to three cycles, with a maximum adsorption efficiency of 97%. This composite showed a multilayer adsorption process that was led by electrostatic attraction in alkaline media and/or cation exchange in acidic media [22]. According to Foroutan et al. [31], the nanocomposite of montmorillonite/graphene oxide/$CoFe_2O_4$ showed a high adsorption capacity of 97.26 mg/g for methyl violet in textile effluents. The adsorbent efficiency of the composite decreased in the acidic medium. Regardless of pH, the adsorption occurs via an electrostatic interaction between the dye and the composite. A porous nanosheet prepared from montmorillonite (MPS) had the potential to remove Congo red from wastewater with a maximum adsorption capacity of 598.31 mg/g. Further, it can be recycled and applied to a wide array of wastewater effluents. The adsorption mechanisms in the process include the formation of hydrogen bonds and surface hydroxyl complexation [82]. Şenol et al. [67] have prepared a chitosan-kaolin composite cross-linked with epichlorohydrin and tripolyphosphate that can remove auramine O (AO) dye from industrial effluents with a maximum adsorption capacity of 0.118 mol/kg.

The adsorbent potential of the composite was restored by 88% after five consecutive adsorption/desorption cycles. Under a basic medium, an antibacterial xanthan gum with poly(vinylimidazole) (XG-g-PVI) and montmorillonite nanocomposite removed malachite green dye with a 99.99% adsorption capacity. Further, the nanocomposite inhibited the growth of commonly found pathogenic bacteria, *E. coli* and *Staphylococcus aureus* in water. The adsorption efficiency of the composite increased as a result of the cumulative effect of several interactive forces such as electrostatic, H-bonding, and π-π interactions between nanocomposite surfaces and dye [23].

3.2 Pharmaceutical Products

The global consumption of pharmaceutical products has increased rapidly in recent years [13, 33]. Hospital effluents, household pharmaceuticals through municipal wastewaters, and discharge effluents from livestock farms and aquaculture are the major sources of pharmaceutical products in the environment [33]. Clay-biochar composites made of clay minerals (e.g., Na-montmorillonite or Na-bentonite) and solid biowaste biochar have been shown to be effective at removing antibiotics such as ciprofloxacin and tetracycline under alkaline conditions [9, 60]. Thermally activated bentonite (TB) showed the highest removal efficiency of tetracycline, 98% at pH 3, compared to 52% for natural bentonite. The tetracycline adsorption mechanism of TB occurred in three ways: ion exchange by the intercalation of tetracycline into the interlayer space of TB, electrostatic interactions between negative binding sites on surface and the cations of tetracycline, and complexation of tetracycline on the edge sites of TB [47]. Another study by Gopal et al. [32] showed that bentonite-Fe/Pd composites can remove tetracycline from wastewater effluents with 95% efficiency. The composite was reusable up to its fourth cycle and showed less toxicity towards aquatic microalgae. Tong et al. [71] observed a better removal of 17β-estradiol (E2) (oestrogen contaminant) using montmorillonite-modified biochar with wheat straw composite, 62.89 mg/g, compared to montmorillonite-modified biochar with cow manure composite, 41.02 mg/g. A bentonite-nanotitanium oxide chitosan composite efficiently removed two classes of antibiotics, including levofloxacin and ceftriaxone, from drinking water. The removal efficiencies were further enhanced with the increase in nanocomposite mass [48]. Montmorillonite clay pillared with titanium oxides was capable of adsorbing a wide range of pharmaceutical compounds, including amoxicillin, diclofenac sodium (DIF-S), imipramine (IMP), and paracetamol, in wastewater effluents. Compared to unmodified montmorillonite, modified montmorillonite showed remarkable removal efficiencies for these compounds [16]. Beside the application of bentonite and montmorillonite and their composites, a recent review by Hacıosmanoğlu et al. [33] mentioned the application potential of illite, halloysite, kaolinite, rectorite, sepiolite, smectite, stevensite, and vermiculite on the removal of antibiotics.

3.3 Hydrocarbons

A nanocomposite that is composed of montmorillonite and a cationic surfactant (cetyltrimethylammonium bromide) with sodium alginate was capable of removing three polycyclic aromatic hydrocarbons (PAHs) (acenaphthene, fluorene, and phenanthrene) from an aqueous solution via a multilayer adsorption process. In addition, the composite was recyclable and biodegradable [20]. A recent study by Ewis et al. [27] developed two magnetite bentonite-based adsorbents combined with reduced graphene and multiwall carbon nanotubes that can efficiently remove diesel oil from waste effluents. However, magnetite bentonite combined with multiwall carbon nanotube composites has shown high efficiency compared to the reduced graphene composite, despite the increase in diesel oil content. The study identified four possible mechanisms for oil removal, including chemical, hydrophobic, π-π, and electrostatics interactions between the composite and oil [27].

3.4 Trace Elements

The high adsorption and cation exchange capacities of clay minerals decrease the bioavailability of trace elements in soil [21]. A recently published review described that the type of clay affects its metal ion affinity. For instance, montmorillonite exhibited selective adsorption towards Cu^{2+} and Cr^{3+}, whereas kaolinite and illite exhibited adsorption towards Cd^{2+}, Pb^{2+}, and Zn^{2+} [79]. Wang et al. [76] demonstrated that modified clay minerals adsorbents (e.g., medical stone modified with a thiol-based material) significantly reduced oxide-bound Hg and MeHg and improved Hg and MeHg retention in soil. Kaolinite and vermiculite clays have the potential to immobilize As, Cd, and Pb and reduce the plants' availability. Further, the acidified amendments have significantly reduced the plant availability of As and Cd [72]. Composites of nanoclays and almond biochar and nanoclays with walnut shell biochar have reduced the leaching of soil Cd and Cu contents from 0.607 to 0.350 and from 0.176 to 0.127, respectively, under alkaline conditions [50]. According to Dong et al. [21], tourmaline clay combined with humic acid adsorbed vanadium from soil via complexation, ion exchange, and adsorption.

Natural bentonite clay activated using nitric acid (Activated bentonite clay) has the potential to remove trace elements (Fe^{2+}, Ni^{2+}, Zn^{2+}) from pharmaceutical effluents more efficiently compared to natural bentonite clay due to its high surface area, porosity, and availability of sorption sites. Further, the strong ionic and electrostatic interactions between trace elements and activated bentonite have resulted in the formation of several adsorption layers to increase their efficiencies [36]. Composites made from the pyrolysis of cigarette factory wastes with bentonite (biochar bentonite) efficiently removed 99.20% of Pb from wastewater through adsorption and electrostatic attraction between Pb and minerals [62]. Song et al. [69] reported about 241% higher adsorption of Zn^{2+} in wastewater from montmorillonite-modified biochar composite than biochar alone, due to electrostatic interaction between the negative charge of the interlayers and Zn^{2+}, ion exchange, and surface complexation. Similarly, Jing et al. [39] discovered that Bentonite-modified biochar (*Alternanthera philoxeroides*) composite had higher Cd^{2+} adsorption (36.9 mg/g) than bentonite and biochar alone. Another study done by Izosimova et al. [37] revealed that the quantity of Cu^{2+} ions sorbed by Na-bentonite was higher compared to Na-bentonite modified with Al keggin cations. During the sorption process, Cu^{2+} and Na^{+} cations are exchanged. Further, the treatment of Na-bentonite modified with Al keggin cations with humic acid increased the Cu^{2+} ion adsorption and was similar to the quantity adsorbed by Na-bentonite. Thermo-exfoliated vermiculite removed Cr^{6+} efficiently (2.81 mol/g) compared to vermiculite irradiated with microwave radiation (0.001 mol/g) at neutral pH [49].

The adsorption capacities shown by the biocomposite synthesized from clay (CCB) and cellulose for Pb^{2+} and Cd^{2+} were 389.78 mg/g and 115.96 mg/g, respectively. Furthermore, the adsorption activity of CCB in fixed-bed columns was investigated. It has been confirmed that the CCB can be effectively reused more than four times to remove Pb and Cd from contaminated water [1]. A composite made from molybdenum disulfide and bentonite (MoS_2/Bentonite) exhibited a maximum Cd^{2+} adsorption capacity of 89.45 mg/g via a chemical adsorption process [46]. A recent study has prepared ion-imprinted magnetic nanocomposite bentonite (IIPNMB), which can selectively adsorb scandium (Sc^{3+}) from water. The oxyphosphorus functional groups in sodium tripolyphosphate and the hydroxyl and amino functional groups in chitosan have provided active sites for the selective adsorption and complexation of Sc^{3+} with IIPNMB [74].

3.5 Pesticides

Glyphosate and paraquat have a strong affinity for soil with a high clay content [75]. Furthermore, carbaryl and methyl parathion have been shown to bind strongly to montmorillonite [81]. Baigorria et al. [11] have developed chitosan-based hydrogels with organoclay to remove carbendazim and other fungicides from water. A modified bentonite prepared by kegging cations (Al30/bentonite) exhibited a 98% removal efficiency of organochlorine pesticides (heptachlor epoxide, dieldrin, and endrin) from water via a chemisorption mechanism [28]. The addition of clays to pesticides-contaminated soil (organophosphorus pesticides) has increased their adsorption into the soil. Thus, it facilitates pesticides retention in soil by avoiding the percolation of pesticides into below-ground soil layers. Pesticides adsorb into montmorillonite and kaolinite via dipole-induced dipole-type interactions between clay and pesticides [19].

3.6 Other Organic and Inorganic Contaminants

A recent review discussed that the application of modified clay minerals such as surfactant (HDTMA)-modified montmorillonite and amine-modified palygorskite is more efficient in the removal of poly- and perfluoroalkyl substances (PFAS) from contaminated water [52]. Further, the authors have described three main mechanisms, such as hydrophobic interactions, electrostatic interactions, and ligand exchange between hydroxide mineral groups in clay minerals and PFAS that are removed by clay-based adsorbents [52]. Ewis et al. [26] have developed an iron oxide/bentonite nanocomposite (Fe_3O_4/Bt. NC) that can remove 99.5% of 4-nitrophenol, a persistent hazardous organic compound, from wastewater at a higher pH level (pH 11). Further, the study identified that the mechanism of the adsorption process involves both physical and chemical interactions, mainly the electrostatic interaction via Fe–O and Si–O and the formation of new chemical bonds. The multifunctional nanocomposite of Fe_2O_3/bentonite modified by doped TiO_2 synthesized by Cao et al. [14] showed significant adsorption efficiencies against recalcitrant organic pollutants in industrial effluents with excellent reusability. Under neutral conditions, the composite exhibited a maximum adsorption efficiency of 77.36 mg/g for bisphenol A (BPA). An organically modified bentonite with Arquad® 2HT-75 (IBA) and palmitic acid was capable of completely removing perfluorooctane sulfonate (PFOS) and phenanthrene (PHE) and 86.6% of Cu^{2+} from wastewater. The adsorption efficiency of PFOS or PHE in the binary solution was increased due to the presence of Cu^{2+}, which serves as a bridge between the clay surface and organic contaminants [41].

A recent review by Lazaratou et al. [43] revealed that unmodified clays have the capacity to remove nitrate at low to medium levels (1–23 mg/g). In contrast, modified clays and clay composites have shown high nitrate removal rates ranging from 6 to 80.76 mg/g. The authors have identified that the main mechanism of nitrate removal occurs through monolayer chemical adsorption. Further, the review has revealed that the presence of competitive cations and some oxyanions, such as Cl^-, CO_3^{2-}, PO_4^{3-}, and SO_4^{2-}, in clay minerals reduces the nitrate removal efficiency [43]. A commercial clay mineral, K10 montmorillonite modified with Fe^{3+} polyhydroxy cations, efficiently removed phosphate from industrial effluents due to the formation of inner-sphere complexes [44]. Reijonen et al. [64] have applied X-ray computed tomography to improve the physical properties of bentonite samples to increase their sealing and retention properties, which can be used in the disposal of radioactive waste.

3.7 Toxic Gaseous Contaminants

Clay minerals/composites are known to show effective adsorption capacities for gaseous pollutants owing to their distinct structure and susceptibility to modification. Clay minerals such as kaolinite, halloysite, montmorillonite, bentonite, saponite, vermiculite, illite, sepiolite, and palygorskite have the potential to adsorb CO_2, methane, and other volatile organic compounds [73]. Carbon dioxide gas is adsorbed into the clay minerals/composites either by surface sorption or interlayer adsorption, depending on the clay and ion type. For instance, Sato and Hunger [66] revealed that the physical sorption of CO_2 occurred due to the presence of nanocavities on surfaces in the open spaces of saponite clay under ambient conditions. The maximum CO_2 adsorption capacity of Cs-exchanged and tetramethylammonium-exchanged montmorillonite was 1.70 mmol/g [51].

4 Application of Clay-Microbial Interactions in Remediation Technologies

Microbial interactions (microbial cells, their exudates, and enzymes) with clay minerals affect the fate of contaminants. Thus, the application of biomodified clay minerals can be utilized in environmental remediation [30, 81]. These microbial aggregates modify the binding sites of clay minerals/composites to increase their adsorptive properties. For instance, smectite-bacterial composites can bind metal(loid)s such as Cu, Cr, Cd, Pb, Hg, and As while degrading organic pollutants [81]. The extracellular polymeric substances (EPS) in clay minerals have the potential to immobilize trace elements in soil [78]. For example, the adsorption of Cd^{2+} onto EPS-montmorillonite composites was dependent on the weight ratio. Some of the bacteria and fungi have the capacity to excrete metal-complexing metabolites such as carboxylic acids, amino acids, siderophores that bind Fe^{3+}, and phenolic compounds that are connected to ligand-promoted dissolution or complexolysis [30]. As reviewed by Li et al. [45], the attachment of bacteria to kaolinite surfaces may occur through several mechanisms, such as cation bridges, which are facilitated by the release of interlayer metal cations (e.g., calcium and sodium) from smectite particles, the EPS layer, hydrophobic interactions, and protein-binding receptors. For instance, when EPS and montmorillonite interacted, negative surface charges increased, resulting in the formation of additional cadmium ion bridges between EPS and montmorillonite [78]. In addition to EPS, clay minerals that are adsorbed into fungal mycelium also have the potential to enhance the metal adsorption [81].

5 Factors that Influence the Remediation Processes

Designing and selecting effective clay-based adsorbents requires an understanding of the variables that affect the adsorption mechanisms [33]. Several parameters that affect the adsorption capacity and removal efficiency of clays and modified clays are ionic strength, pH, temperature, organic matter content, trace element composition, and pollutant composition [6]. However, depending on the type of contaminant and composites used, different studies have reported contradictory effects of these factors on the adsorption and removal efficiencies. The adsorption efficiency is also determined by the texture (pore size, pore volume, surface area) and surface chemistry (cation exchange capacity, isoelectric point, surface functional groups) of clays/composites [33, 47, 52]. For instance, thermally activated bentonite showed a high adsorption capacity of tetracycline (388.1 mg/g) compared to raw bentonite (156.7 mg/g) as a result of surface modifications [47]. The presence of competing ions, which are either organic or inorganic, affects the contaminant adsorption efficiency of clay-based adsorbents. Furthermore, the ionic strength and cationic and anionic nature of competing ions in the contaminant matrix compete with the targeted pollutant [52]. A recent review has revealed that the adsorption of specific pollutants onto chitosan/bentonite composites is greater in distilled water than in tap water, groundwater, industrial wastewater, or sea water [25]. The presence of multiple types of pollutants that interact with the binding sites of composites is the main reason for the reduction of the adsorption capacity in industrial wastewater [48]. Temperature and pH are two critical factors that influence adsorption efficiency. At high temperatures and pH, the adsorption process increased or decreased depending on the nature of the contaminant and medium [33]. The surface charges of clay minerals mainly depend on pH, and as a result, the cation exchange capacity of clay varies with pH. Most of the recorded bentonite/metal oxide composites have shown their optimum adsorption capacities at pH values between 5 and 8. The adsorption capacities of montmorillonite/metal oxide composites changed as the temperature changed. For example, Chauhan et al. [16] discovered that Ti-pillared montmorillonite adsorbed imipramine and diclofenac sodium at high temperatures but not amoxicillin or paracetamol. A recent review by Mukhopadhyay et al. [52] revealed that factors such as high temperature and pH, the presence of competing anions, and natural organic matter have reduced the adsorption efficiency of PFAS by clay-based adsorbents. Besides that, the physiochemical properties of both pollutants and composites are directly linked with the adsorption mechanism [25].

6 Conclusion and Future Remarks

As the fate and adverse effects of many contaminants could not be predicted earlier, proper remediation measures are required to minimize the spread and persistence of contaminants and restore ecosystem functions. The ubiquitous nature, high surface area and charge ratio, high porosity, and other physiochemical properties of clays and clay minerals make them more appropriate for remediation purposes. Many studies have revealed that clay minerals are economically feasible and have a higher contaminant adsorption and removal capacity. The absorption capacities of these clays have been further enhanced by combining one or more materials, known as clay-based composites, using more advanced techniques (e.g., clay-based nanocomposites). Although ongoing scientific interest is focused on enhancing the efficiency of the adsorption process of composites, many of the studies have been implemented in laboratory-scale batch reactors, and conclusions have been drawn based on that. Thus, pilot-scale studies beyond laboratories are scarce in many instances to predict their performance and adsorption efficiencies and approve their applicability. Furthermore, considerable researches have been conducted on the role of clay minerals/composites in the removal of different types of contaminants from polluted water sources compared to soil. Hence, it is necessary to consider the application potential of clay minerals/composites in the remediation of contaminated soil. Further, new composites should be developed for a broad range of contaminants with efficient adsorption efficiency. According to the available literature, bentonite and montmorillonite-based composites have shown high contaminant removal efficiencies compared to other types of clay composites and are found to be the widely applied material for a broad range of contaminants. Multiple factors, such as solution pH, surface charge, competing cations and anions in the composite, and the contaminant source, affect the efficiency and mechanisms of adsorption. The selection of suitable clay mineral/ composites requires careful consideration. Apart from the adsorption efficiency, when using composites on a large scale, it is vital to consider their recyclability. However, only a few studies have investigated the reusability of composites. Therefore, when developing new advanced clay-based composites, their reusability should also be determined. In addition, appropriate measures should be taken for the safe disposal of spent clay adsorbents due to their high toxicity. Further, when incorporating substances such as surfactants, organic acids as modifiers, or synthesizing composites, their impacts on living organisms in the polluted sites should be considered. Therefore, it is necessary to evaluate the toxicity of those chemically modified clays and composites prior to field application. Moreover, future research should be focused on bio-based and non-toxic modifiers.

References

1. Abu-Danso, E., et al.: Synthesis of clay-cellulose biocomposite for the removal of toxic metal ions from aqueous medium. J. Hazard. Mater. **381**, 120871 (2020). https://doi.org/10.1016/j.jhazmat.2019.120871
2. Ahmadi, A., et al.: Montmorillonite clay/starch/$CoFe_2O_4$ nanocomposite as a superior functional material for uptake of cationic dye molecules from water and wastewater. Mater. Chem. Phys. **284**, 126088 (2022). https://doi.org/10.1016/j.matchemphys.2022.126088
3. Ain, Q.U., et al.: Fabrication of magnetically separable 3-acrylamidopropyltrimethylammonium chloride intercalated bentonite composite for the efficient adsorption of cationic and anionic dyes. Appl. Surf. Sci. **514**, 145929 (2020). https://doi.org/10.1016/j.apsusc.2020.145929
4. Ain, Q.U., et al.: Superior dye degradation and adsorption capability of polydopamine modified Fe_3O_4-pillared bentonite composite. J. Hazard. Mater. **397**, 122758 (2020). https://doi.org/10.1016/j.jhazmat.2020.122758
5. Almahri, A.: The solid-state synthetic performance of bentonite stacked manganese ferrite nanoparticles: adsorption and photo-fenton degradation of MB dye and antibacterial applications. J. Mater. Res. Technol. **17**, 2935–2949 (2022). https://doi.org/10.1016/j.jmrt.2022.02.052

6. Amari, A., et al.: Clay-polymer nanocomposites: preparations and utilization for pollutants removal. Materials **14**(6), 1365 (2021). https://doi.org/10.3390/ma14061365
7. Antonelli, R., et al.: Adsorption of ciprofloxacin onto thermally modified bentonite clay: experimental design, characterization, and adsorbent regeneration. J. Environ. Chem. Eng. **8**(6), 104553 (2020). https://doi.org/10.1016/j.jece.2020.104553
8. Arif, M., et al.: Synthesis, characteristics and mechanistic insight into the clays and clay minerals-biochar surface interactions for contaminants removal-—a review. J. Clean. Prod. **310**, 127548 (2021). https://doi.org/10.1016/j.jclepro.2021.127548
9. Ashiq, A., et al.: Sorption process of municipal solid waste biochar-montmorillonite composite for ciprofloxacin removal in aqueous media. Chemosphere **236**, 124384 (2019). https://doi.org/10.1016/j.chemosphere.2019.124384
10. Ashraf, A., et al.: Recent trends in advanced oxidation process-based degradation of erythromycin: pollution status, eco-toxicity and degradation mechanism in aquatic ecosystems. Sci. Total Environ. **772**, 145389 (2021). https://doi.org/10.1016/j.scitotenv.2021.145389
11. Baigorria, E., Fraceto, L.F.: Novel nanostructured materials based on polymer/organic-clay composite networks for the removal of carbendazim from waters. J. Clean. Prod. **331**, 129867 (2022). https://doi.org/10.1016/j.jclepro.2021.129867
12. Barakan, S., Aghazadeh, V.: The advantages of clay mineral modification methods for enhancing adsorption efficiency in wastewater treatment: a review. Environ. Sci. Pollut. Res. **28**(3), 2572–2599 (2021). https://doi.org/10.1007/s11356-020-10985-9
13. Bhattacharyya, P., et al.: Advancement towards antibiotic remediation: heterostructure and composite materials. Chem Select **6**(29), 7323–7345 (2021). https://doi.org/10.1002/slct.202100436
14. Cao, Y., et al.: Green synthesis of reusable multifunctional γ-Fe2O3/bentonite modified by doped TiO_2 hollow spherical nanocomposite for removal of BPA. Sci. Total Environ. **708**, 134669 (2020). https://doi.org/10.1016/j.scitotenv.2019.134669
15. Chang, Y.S., et al.: Adsorption of Cu (II) and Ni (II) ions from wastewater onto bentonite and bentonite/GO composite. Environ. Sci. Pollut. Res. Int. **27**(26), 33270–33296 (2020). https://doi.org/10.1007/s11356-020-09423-7
16. Chauhan, M., et al.: Ti-pillared montmorillonite clay for adsorptive removal of amoxicillin, imipramine, diclofenac-sodium, and paracetamol from water. J. Hazard. Mater. **399**, 122832 (2020). https://doi.org/10.1016/j.jhazmat.2020.122832
17. Chen, D., et al.: Photocatalytic degradation of organic pollutants using TiO2-based photocatalysts: a review. J. Clean. Prod. **268**, 121725 (2020). https://doi.org/10.1016/j.jclepro.2020.121725
18. Chen, Z., et al.: Application of surfactant modified montmorillonite with different conformation for photo-treatment of perfluorooctanoic acid by hydrated electrons. Chemosphere **235**, 1180–1188 (2019). https://doi.org/10.1016/j.chemosphere.2019.07.032
19. Copaja, S.V., Gatica-Jeria, P.: Effects of clay content in soil on pesticides sorption process. J. Chil. Chem. Soc. **66**(1), 5086–5092 (2021). https://doi.org/10.4067/S0717-97072021000105086
20. Dai, W.J., et al.: Adsorption of polycyclic aromatic hydrocarbons from aqueous solution by organic montmorillonite sodium alginate nanocomposites. Chemosphere **251**, 126074 (2020). https://doi.org/10.1016/j.chemosphere.2020.126074
21. Dong, Y., et al.: Remediation of vanadium-contaminated soils by the combination of natural clay mineral and humic acid. J. Clean. Prod. **279**, 123874 (2021). https://doi.org/10.1016/j.jclepro.2020.123874
22. El-Kousy, S.M., et al.: Chitosan/montmorillonite composites for fast removal of methylene blue from aqueous solutions. Mater. Chem. Phys. **254**, 123236 (2020). https://doi.org/10.1016/j.matchemphys.2020.123236
23. Elella, M.H.A., et al.: Innovative bactericidal adsorbents containing modified xanthan gum/montmorillonite nanocomposites for wastewater treatment. Int. J. Biol. Macromol. **167**, 1113–1125 (2021). https://doi.org/10.1016/j.ijbiomac.2020.11.065

24. Eltaweil, A., et al.: Mesoporous magnetic biochar composite for enhanced adsorption of malachite green dye: characterization, adsorption kinetics, thermodynamics and isotherms. Adv. Powder Technol. **31**(3), 1253–1263 (2020). https://doi.org/10.1016/j.apt.2020.01.005
25. Ewis, D., et al.: Adsorption of organic water pollutants by clays and clay minerals composites: a comprehensive review. Appl. Clay Sci. **229**, 106686 (2022). https://doi.org/10.1016/j.clay.2022.106686
26. Ewis, D., et al.: Adsorption of 4-nitrophenol onto iron oxide bentonite nanocomposite: process optimization, kinetics, isotherms and mechanism. Int. J. Environ. Res. **16**(2), 1–13 (2022). https://doi.org/10.1007/s41742-022-00402-z
27. Ewis, D., et al.: Enhanced removal of diesel oil using new magnetic bentonite-based adsorbents combined with different carbon sources. Water Air Soil Pollut. **233**(195), 1–19 (2022). https://doi.org/10.1007/s11270-022-05641-6
28. Farghali, R., et al.: Adsorption of organochlorine pesticides on modified porous Al30/bentonite: kinetic and thermodynamic studies. Arab. J. Chem. **13**(8), 6730–6740 (2020). https://doi.org/10.1016/j.arabjc.2020.06.027
29. Fei, F., et al.: Facile solid-state synthesis of Fe_3O_4/kaolinite nanocomposites for enhanced dye adsorption. J. Solid State Chem. **291**, 121655 (2020). https://doi.org/10.1016/j.jssc.2020.121655
30. Fomina, M., Skorochod, I.: Microbial interaction with clay minerals and its environmental and biotechnological implications. Minerals **10**(10), 861 (2020). https://doi.org/10.3390/min10100861
31. Foroutan, R., et al.: Performance of montmorillonite/graphene oxide/$CoFe_2O_4$ as a magnetic and recyclable nanocomposite for cleaning methyl violet dye-laden wastewater. Adv. Powder Technol. **31**(9), 3993–4004 (2020). https://doi.org/10.1016/j.apt.2020.08.001
32. Gopal, G., et al.: Green synthesized Fe/Pd and in-situ Bentonite-Fe/Pd composite for efficient tetracycline removal. J. Environ. Chem. Eng. **8**(5), 104126 (2020). https://doi.org/10.1016/j.jece.2020.104126
33. Hacıosmanoğlu, G.G., et al.: Antibiotic adsorption by natural and modified clay minerals as designer adsorbents for wastewater treatment: a comprehensive review. J. Environ. Manage. **317**, 115397 (2022). https://doi.org/10.1016/j.jenvman.2022.115397
34. Heidari, A., et al.: A systematic review of clay-based photocatalysts for emergent micropollutants removal and microbial inactivation from aqueous media: status and limitations. J. Environ. Chem. Eng. **10**(6), 108813 (2022). https://doi.org/10.1016/j.jece.2022.108813
35. Hnamte, M., Pulikkal, A.K.: Clay-polymer nanocomposites for water and wastewater treatment: a comprehensive. Chemosphere 135869 (2022). https://doi.org/10.1016/j.chemosphere.2022.135869
36. Ibigbami, T.B., et al.: Pristine and activated bentonite for toxic metal removal from wastewater. Water Pract. Technol. **17**(3), 784–797 (2022). https://doi.org/10.2166/wpt.2022.018
37. Izosimova, Y., et al.: Sorption of Cu^{2+} Ions by bentonite modified with Al Keggin cations and humic acid in solutions with pH 4.5. Minerals **10**(12), 1121 (2020). https://doi.org/10.3390/min10121121
38. Janeni, J., Adassooriya, N.M.: Clays and clay polymer composites for electrokinetic remediation of soil. In: Ribeiro, A.B., Prasad, M.N.V. (Eds.). Electrokinetic Remediation for Environmental Security and Sustainability, pp. 587–602. John Wiley & Sons, Ltd., (2021). https://doi.org/10.1002/9781119670186.ch23
39. Jing, Y., et al.: Removal of Cd (II) from aqueous solution by clay-biochar composite prepared from Alternanthera philoxeroides and bentonite. BioRes. **15**(1), 598–615 (2020). https://doi.org/10.15376/biores.15.1.598-615
40. Kárászová, M., et al.: Membrane removal of emerging contaminants from water: which kind of membranes should we use? Membranes **10**(11), 305 (2020). https://doi.org/10.3390/membranes10110305
41. Khodabakhshloo, N., et al.: Organically functionalized bentonite for the removal of perfluorooctane sulfonate, phenanthrene and copper mixtures from wastewater. Appl. Clay Sci. **200**, 105883 (2021). https://doi.org/10.1016/j.clay.2020.105883

42. Kumari, N., Mohan, C.: Basics of clay minerals and their characteristic properties. In: Nascimento, G.M.D. (Ed.) Clay and Clay Minerals, IntechOpen, 1–29. London (2021). https://doi.org/10.5772/intechopen.97672
43. Lazaratou, C., et al.: The role of clays, clay minerals and clay-based materials for nitrate removal from water systems: a review. Appl. Clay Sci. **185**, 105377 (2020). https://doi.org/10.1016/j.clay.2019.105377
44. Leite, S.T., et al.: Fe (III)-polyhydroxy cations supported onto K10 montmorillonite for removal of phosphate from waters. Heliyon **6**(4), e03868 (2020). https://doi.org/10.1016/j.heliyon.2020.e03868
45. Li, G.L., et al.: Interactions between microorganisms and clay minerals: new insights and broader applications. Appl. Clay Sci. **177**, 91–113 (2019). https://doi.org/10.1016/j.clay.2019.04.025
46. Li, W., et al.: MoS_2/Bentonite prepared by a facile method for efficient removal of Cd^{2+} from aqueous solution. J. Alloys Compd. **907**, 164508 (2022). https://doi.org/10.1016/j.jallcom.2022.164508
47. Maged, A., et al.: Tuning tetracycline removal from aqueous solution onto activated 2: 1 layered clay mineral: characterization, sorption and mechanistic studies. J. Hazard. Mater. **384**, 121320 (2020). https://doi.org/10.1016/j.jhazmat.2019.121320
48. Mahmoud, M.E., et al.: Enhanced adsorption of Levofloxacin and Ceftriaxone antibiotics from water by assembled composite of nanotitanium oxide/chitosan/nano-bentonite. Mater. Sci. Eng. **108**, 110199 (2020). https://doi.org/10.1016/j.msec.2019.110199
49. Marcos, C., et al.: Modified vermiculite as adsorbent of hexavalent chromium in aqueous solution. Minerals **10**(9), 749 (2020). https://doi.org/10.3390/min10090749
50. Matin, N.H., et al.: Synergistic immobilization of potentially toxic elements (PTEs) by biochar and nanoparticles in alkaline soil. Chemosphere **241**, 124932 (2020). https://doi.org/10.1016/j.chemosphere.2019.124932
51. Mendel, N., et al.: Interlayer cation-controlled adsorption of carbon dioxide in anhydrous montmorillonite clay. J. Phys. Chem. C **125**(49), 27159–27169 (2021). https://doi.org/10.1021/acs.jpcc.1c06746
52. Mukhopadhyay, R., et al.: Natural and engineered clays and clay minerals for the removal of poly-and perfluoroalkyl substances from water: State-of-the-art and future perspectives. Adv. Colloid Interface Sci. **297**, 102537 (2021). https://doi.org/10.1016/j.cis.2021.102537
53. Murtić, S., et al.: In situ immobilisation of heavy metals in soils using natural clay minerals. Plant Soil Environ. **66**(12), 632–638 (2020). https://doi.org/10.17221/371/2020-PSE
54. Najafi, H., et al.: A comprehensive study on modified-pillared clays as an adsorbent in wastewater treatment processes. Process Saf. Environ. Prot. **147**, 8–36 (2021). https://doi.org/10.1016/j.psep.2020.09.028
55. Naz, A., Chowdhury, A.: Nano clay-polymer composite for water treatment. In: Advanced Applications of Micro and Nano Clay II: Synthetic Polymer Composites, Materials Research Foundations, pp. 129–152 (2022). https://doi.org/10.21741/9781644902035-6
56. Osuna, F.J., et al.: Improved stability of design clay minerals at high temperature: a comparison study with natural ones. Ceram. Int. **49**(3), 5279–5291 (2022). https://doi.org/10.1016/j.ceramint.2022.10.046
57. Otunola, B.O., Ololade, O.O.: A review on the application of clay minerals as heavy metal adsorbents for remediation purposes. Environ. Technol. Innov. **18**, 100692 (2020). https://doi.org/10.1016/j.eti.2020.100692
58. Oyewo, O.A., et al.: Metal oxide-cellulose nanocomposites for the removal of toxic metals and dyes from wastewater. Int. J. Biol. Macromol. **164**, 2477–2496 (2020). https://doi.org/10.1016/j.ijbiomac.2020.08.074
59. Pareek, P., Ledwani, L.J.I.W.T.: Synthesis and Applications of Polymer–Nano Clay Composites in Wastewater Treatment: A Review. In: Karchiyappan, T., et al. (eds.). Industrial Wastewater Treatment, Springer, Cham, 237–256 (2022). https://doi.org/10.1007/978-3-030-98202-7_9
60. Premarathna, K., et al.: Clay-biochar composites for sorptive removal of tetracycline antibiotic in aqueous media. J. Environ. Manage. **238**, 315–322 (2019). https://doi.org/10.1016/j.jenvman.2019.02.069

61. Rai, P.K.: Novel adsorbents in remediation of hazardous environmental pollutants: progress, selectivity, and sustainability prospects. Clean. Mater. **3**, 100054 (2022). https://doi.org/10.1016/j.clema.2022.100054
62. Ramola, S., et al.: Improved lead removal from aqueous solution using novel porous bentonite- and calcite-biochar composite. Sci. Total Environ. **709**, 136171 (2020). https://doi.org/10.1016/j.scitotenv.2019.136171
63. Ray, J.R., et al.: Polymer-clay composite geomedia for sorptive removal of trace organic compounds and metals in urban stormwater. Water Res. **157**, 454–462 (2019). https://doi.org/10.1016/j.watres.2019.03.097
64. Reijonen, H.M., et al.: Benefits of applying X-ray computed tomography in bentonite based material research focussed on geological disposal of radioactive waste. Environ. Sci. Pollut. Res. **27**(31), 38407–38421 (2020). https://doi.org/10.1007/s11356-020-08151-2
65. Sarkar, B., et al.: Modified clay minerals for environmental applications. In: Mercurio, M., et al. (Eds.). Modified Clay and Zeolite Nanocomposite Materials, pp. 113–127. Elsevier (2019). https://doi.org/10.1016/B978-0-12-814617-0.00003-7
66. Sato, K., Hunger, M.: Carbon dioxide adsorption in open nanospaces formed by overlap of saponite clay nanosheets. Commun. Chem. **3**(91), 1–7 (2020). https://doi.org/10.1038/s42004-020-00346-5
67. Şenol, Z.M., et al.: Epichlorohydrin and tripolyphosphate-crosslinked chitosan–kaolin composite for Auramine O dye removal from aqueous solutions: experimental study and DFT calculations. Int. J. Biol. Macromol. **199**, 318–330 (2022). https://doi.org/10.1016/j.ijbiomac.2022.01.008
68. Shigidi, I., et al.: Waste engine oil remediation using low cost natural clay absorbent material. Int. J. Eng. **33**(2), 178–185 (2020). https://doi.org/10.5829/IJE.2020.33.02B.01
69. Song, J., et al.: Preparation of montmorillonite modified biochar with various temperatures and their mechanism for Zn ion removal. J. Hazard. Mater. **391**, 121692 (2020). https://doi.org/10.1016/j.jhazmat.2019.121692
70. Thiebault, T.: Raw and modified clays and clay minerals for the removal of pharmaceutical products from aqueous solutions: state of the art and future perspectives. Crit. Rev. Environ. Sci. **50**(14), 1451–1514 (2020). https://doi.org/10.1080/10643389.2019.1663065
71. Tong, X., et al.: Function of agricultural waste montmorillonite-biochars for sorptive removal of 17β-estradiol. Bioresour. Technol. **296**, 122368 (2020). https://doi.org/10.1016/j.biortech.2019.122368
72. Vejvodova, K., et al.: Effect of clay on the fractions of potentially toxic elements in contaminated soil. Soil Water Res. **16**(1), 1–10 (2020). https://doi.org/10.17221/13/2020-SWR
73. Wal, K., et al.: Application of clay minerals and their derivatives in adsorption from gaseous phase. Appl. Clay Sci. **215**, 106323 (2021). https://doi.org/10.1016/j.clay.2021.106323
74. Wang, C., et al.: Synthesis of environmental-friendly ion-imprinted magnetic nanocomposite bentonite for selective recovery of aqueous Sc (III). J. Colloid Interface Sci. **630**, 738–750 (2023). https://doi.org/10.1016/j.jcis.2022.10.161
75. Wang, M., et al.: Montmorillonites can tightly bind glyphosate and paraquat reducing toxin exposures and toxicity. ACS Omega **4**(18), 17702–17713 (2019). https://doi.org/10.1021/acsomega.9b02051
76. Wang, Y., et al.: Modified clay mineral: a method for the remediation of the mercury-polluted paddy soil. Ecotoxicol. Environ. Saf. **204**, 111121 (2020). https://doi.org/10.1016/j.ecoenv.2020.111121
77. Yan, B., et al.: Molecular mechanisms of per-and polyfluoroalkyl substances on a modified clay: a combined experimental and molecular simulation study. Water Res. **184**, 116166 (2020). https://doi.org/10.1016/j.watres.2020.116166
78. Yan, S., et al.: Enhancement of cadmium adsorption by EPS-montmorillonite composites. Environ. Pollut. **252**, 1509–1518 (2019). https://doi.org/10.1016/j.envpol.2019.06.071
79. Yingying, S., et al.:Application of clay minerals in remediation of heavy metal pollution in soil. In: International Conference of Recent Trends in Environmental Sustainability and Green Technologies. EDP Sci. 01011 (2020). https://doi.org/10.1051/e3sconf/202020401011

80. Yu, F., et al.: Recent progress on metal-organic framework-derived porous carbon and its composite for pollutant adsorption from liquid phase. Chem. Eng. J. **405**, 126960 (2021). https://doi.org/10.1016/j.cej.2020.126960
81. Zhang, L., et al.: Microbial biomodification of clay minerals. Adv. Appl. Microbiol. **114**, 111–139 (2021). https://doi.org/10.1016/bs.aambs.2020.07.002
82. Zhang, Z., et al.: Adsorption properties of millimeter porous spheres constructed by montmorillonite nanosheets. Appl. Clay Sci. **216**, 106324 (2022). https://doi.org/10.1016/j.clay.2021.106324

Clay Composites: Physicochemical Characterization

Fábio Carvalho Nunes, Cláudia Cseko Nolasco de Carvalho, Lander de Jesus Alves, and Majeti Narasimha Vara Prasad

Abstract Clay compounds have been used by human societies since time immemorial, because they are abundant in nature, smaller than 4 microns, adherent, plastic, malleable, have ion exchange capacity and affinity with water. Due to their physical and chemical properties, they are used in agriculture, livestock, industry, commerce, tourism and the environment for the development of services and products such as bricks, crockery, paints, pharmaceuticals, agricultural inputs and natural filters. The clay composition of an environment depends on the rock that gave rise to it, weathering and pedogenesis, with the following groups standing out: kaolinite-serpentine, talc-pyrophyllite, mica, vermiculite, smectite, chlorite and sepiolite-palygorskite. Each of these groups has specific physicochemical properties, which will direct them to certain uses. Proper use requires prior characterization, so in this chapter we will discuss the main types of clay compounds, their structure, formation, occurrence, mineralogical and physicochemical characteristics and their environmental importance.

Keywords Clay compounds · Electrostatic interaction · Ion exchange capacity (IEC) · Adsorption

---

F. C. Nunes (✉)
Academic Department, Federal Institute Baiano (IF BAIANO), Santa Inês, Bahia, Brazil
e-mail: fabio.nunes@ifbaiano.edu.br

C. C. N. de Carvalho
Department of Biology, State University of Alagoas, Santana Do Ipanema, Alagoas, Brazil

L. de Jesus Alves
State University of Santa Cruz (UESC), Ilhéus, Bahia, Brazil

M. N. V. Prasad
School of Life Sciences, University of Hyderabad, Hyderabad, India

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_2

1 Introduction

Clay minerals are natural compounds, consisting essentially of very small crystalline particles of hydrated aluminum, iron and magnesium silicates, which when moistened with water acquire a certain plasticity. In addition to Al, Fe and Mg, clay minerals can contain other elements in their structure, such as alkaline and earth alkaline, making them diverse and complex.

Clay minerals normally refer to phyllosilicate minerals that occur in clays (less than 4 microns), according to the Wentworth scale [61], and in the clay fraction (less than 2 microns). Some authors restrict the concept of clay minerals to secondary phyllosilicates from soil weathering [39], however, the Clay Minerals Society (CMS) and the Association Internacionale pour l'Étude des Argiles (AIPEA) consider that clay minerals comprise phyllosilicate minerals and any other minerals smaller than 4 microns that give clay plasticity and harden by drying or calcination [25, 30], a concept adopted in this chapter.

Clay compounds have been used by human societies since time immemorial, because they are abundant in nature, smaller than 4 microns, adherent, plastic, malleable, have ion exchange capacity and affinity with water. Due to their physical and chemical properties, they are used in agriculture, livestock, industry, commerce, tourism and the environment for the development of services and products such as bricks, crockery, paints, pharmaceuticals, agricultural inputs and natural filters, so it is of interest from various areas of knowledge.

In the Clay Flower scheme (Fig. 1), the interrelationship between clay science (clay mineralogy) and related sciences and clay technologies can be observed. Clay mineralogy studies the morphology, crystallography, chemistry and physics of clay compounds. The knowledge developed by the science of clays subsidizes, for example, geology in the understanding of surface processes such as weathering and erosion, helping to understand the current dynamics of the landscape, in the reconstitution of paleocenes and in the elaboration of future forecasts.

Clay science supports soil science in understanding the genesis and evolution of soils, their morphological, physical and chemical attributes, susceptibility to degradation and mass movements. Such knowledge helps in more efficient and sustainable uses by engineering, environmental sciences and different industrial sectors, such as the oil, chemical, pharmaceutical and space industries.

The clay composition of an environment depends on the original rock, weathering, pedogenesis, stages of stability, transformations and neoformations, highlighting the following groups of phyllosilicates: kaolinite-serpentine, talc-pyrophyllite, mica, vermiculite, smectite, chlorite and sepiolite—palygorskite. Phyllosilicates can be classified according to layer type and charge, interlayer material type, octahedral sheet type and chemical composition (Table 1) [5]. Each of these groups has specific physical and chemical properties, which will direct them to certain uses.

Proper use requires previous characterization, so in this chapter we will discuss the main groups of phyllosilicates, as they are the most common clay compounds, as well as their structure, formation, occurrence, mineralogical, physical, chemical characteristics and their environmental importance.

Fig. 1 Clay flower scheme—interrelationships between clay science, related sciences and clay technologies

2 Fundamentals, Structure and Properties of Phyllosilicates

According to the Clay Minerals Society (CMS), clay minerals are phyllosilicates and other minerals smaller than 4 microns that give clay plasticity. However, as phyllosilicates are the most common clay minerals, our focus will be on them. The word phyllosilicate comes from the Greek phylon, which means leaf, because the constituents of this group have a flattened habit, basal cleavage and the cleavage layers are normally plastic.

The structures of phyllosilicates are basically formed by the superposition of sheets of silicon tetrahedra (SiO_4), where three of the four coordinated oxygens are shared with neighboring tetrahedra, forming the so-called tetrahedral sheet (T) or siloxane (Fig. 2a). Tetrahedral sheets unite with aluminum octahedral sheets of the gibbsite ($Al(OH)_3$) or brucite ($Mg(OH)_2$) type (Fig. 2b), giving rise to two families, respectively, trioctahedral and dioctahedral.

Table 1 Classification of phyllosilicates. *Source* Adapted from [9] and [5]

Layer type*	Interlayer	Group[1]	Subgroup[2]	Examples
1:1	None or only H_2O	Kaolinite-Serpentine (x ~ 0)	Kaolinite (D) Serpentine (T)	Kaolinite, halloysite Chrysotile, lizardite
2:1	None	Talc-Pyrophyllite (x ~ 0)	Talc (T) Pyrophyllite (D)	Talc Pyrophyllite
2:1	Unhydrated cations	Mica (x ~ 1)	Mica (T) Mica (D)	Biotite, phlogopite Muscovite, illite
2:1	Hydrated exchangeable cations	Vermiculite (x ~ 0,6–0,9)	Vermiculite (T) Vermiculite (D)	Vermiculite
2:1	Hydrated exchangeable cations	Smectite (x ~ 0,2–0,6)	Smectite (T) Smectite (D)	Saponite, hectorite, sauconite Montmorillonite, beidellite
2:1:1	Hydroxide blade	Chlorite (x variable)	Chlorite (T) Chlorite (D)	Clinochlore Donbassite
2:1 modulada	H_2O	Sepiolite-Palygorskite (x variable)	Sepiolite (T) Palygorskite (D)	Sepiolite Palygorskite

*Refers to the superposition of tetrahedral and octahedral sheets, described in the following item; (1) x = Layer load per unit structural formula based on half unit cell. (2) D = dioctahedral; T = trioctahedral

These are simplified models to facilitate understanding, as they are actually more complex, as demonstrated by Schulze [50], who identified distortions in models with real structures. There are two reasons why real minerals deviate from ideal structures:

(a) atoms are not hard spheres whose closest approximation is determined only by the sum of their radii;

(b) if one tries to join octahedral and tetrahedral sheets constructed with hard spheres, they will not fit together if the spheres representing the oxygen atoms touch each other in the octahedral and tetrahedral sheets. A detailed explanation can be found on pages 25–26 of [50].

The sequence of tetrahedral and octahedral sheets, the existence of ions or compounds between the sheets and the isomorphic substitutions determine the existence of different clay minerals. Clay minerals can be poorly crystallized (allophane) or crystalline, and these can be divided into 1:1 and 2:1 minerals. The union between the layers that form the phyllosilicates occurs by electrostatic bonds between the O and OH ions of adjacent layers in the 1:1 minerals, through cations such as K, Ca and Mg, groups or hydroxy-octahedral sheets positioned in the interlayers of minerals. 2:1 or by van der Waals forces in minerals without net charge [30].

Clay minerals 1:1 are the simplest structures in which only a tetrahedral sheet $(Si_2O_5)^{2-}$ (T) is bonded to a sheet of brucite $Mg_3(OH_6)$ (O) or a sheet of gibbsite

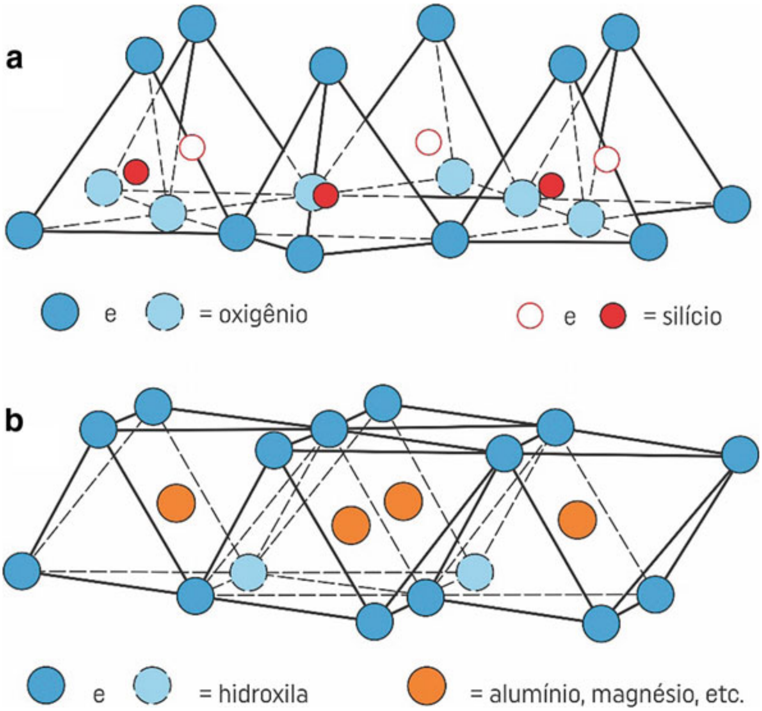


Fig. 2 Models of Si tetrahedrons and Al and Mg octahedrons. **a** Tetrahedrons sharing oxygen and giving rise to the tetrahedral sheet. **b** Octahedrons sharing edges and giving rise to the octahedral blade. *Source* Adapted from [23], pp. 43–44

$Al_2(OH)_6$ (O), generating a T-O structure. Kaolinite is an example of a 1:1 clay mineral where a siloxane sheet (T) joins a gibbsite type sheet (O), another example is serpentine, where a siloxane sheet (T) joins a sheet of type brucita (O) [50, 64].

The junction of the tetrahedral with the octahedral lamina in 1:1 minerals occurs from the positioning of two oxygens corresponding to the vertices of two unshared tetrahedra of the siloxane lamina, in the place of the positions of two of the three hydroxyls that define faces of the octahedrons in the contact of the octahedral (O) with the tetrahedral (T) blade [40, 50, 64].

The 2:1 clay minerals are formed by the continuous superposition of two tetrahedral sheets for each octahedral sheet, as in the cases of talc and pyrophyllite, where in the first case the structure is trioctahedral and in the second dioctahedral. In these structures, the octahedral lamina is arranged between two tetrahedrals and the coupling occurs by replacing the hydroxyl by oxygen at the apex of the tetrahedrons. Of a total of six hydroxyls of each octahedron, either trioctahedral or dioctahedral, four are replaced by the apical oxygens of the tetrahedrons to form the T-O-T structures [64].

Clay minerals 2:1 can be organized into non-expansive and expansive. The expansive capacity of 2:1 minerals and the expansion intensity are related to the layer charge and its tetrahedral or octahedral origin [50], that is, it is associated with the location of the isomorphic substitution. This explains, for example, the non-expansion of micas, the lower expansion of vermiculite in relation to smectite and the lower expansion of beidellite when compared to montmorillonite, as it has an isomorphic octahedral substitution [49]. According to Kampf and Curi [30], the increase in the charge of the layer and its tetrahedral origin facilitate the contraction of the layers at 1 nm by intercalation with K, improving the organization and decreasing the number of water molecules that can be accommodated in the interlayers.

Clay minerals 2:1 normally occur in poorly weathered soils and environments or from parent materials that contain minerals susceptible to chemical weathering. These clay minerals give soils high cation exchange capacity, high plasticity and stickiness.

Physical and chemical characteristics of phyllosilicates are controlled by the structure of minerals through active sites on the surface of the particles, which interact with other substances or with components of the solution in the environment 64. During crystal formation, the dominant cation can be replaced by cations with similar ionic radius and different charge, configuring the substitution and isomorphic and giving rise to net charges.

In the formation of tetrahedra, for example, Si^{+4} can be replaced by Al^{+3}, or in the constitution of octahedra, Al^{+3} can be replaced by Mg^{+2} or Fe^{+2}, creating negative electrical charges on the mineral surface. When Al^{+3}, for example, replaces Mg^{+2} or Fe^{+2} at octahedral sites, positive electrical charges are generated. Charges arising from isomorphic substitutions are permanent, independent of pH.

The electrical charges generated by isomorphic substitution produce very important surface phenomena, such as cation exchange capacity (CEC). The CEC of soils plays a fundamental role in the balance of the environment, which is the retention and availability of nutrients for the plants. The anion exchange capacity (AEC) is another important phenomenon originated through isomorphic substitutions, which together with the CTC will mediate control processes (retention and availability) of ions in the environment.

There are electrical charges generated on the surface of minerals that are variable, but these are not related to isomorphic substitution. They result from reactions between H^+ and O^{2-} ions existing on the surface of mineral particles and commonly occur between clay minerals 1:1, Fe and Al oxides, humus and soil solution, varying according to pH. Table 2 summarizes the origin of negative and positive electrical charges in phyllosilicates.

The phyllosilicates strongly influence the physical and chemical properties of sediments and soils, because they are small particles, have high specific surface and cationic and anion exchange properties. Therefore, they are important for understanding many environmental processes and applying strategies for remediation, restoration and environmental control.

The discovery in the early 1920s that clays are crystalline was key to understanding many of the properties of soils and clays. The crystal structures of phyllosilicates

Table 2 Origin of negative and positive electrical charges in phyllosilicates

Constant electrical charges (Negatives)	Variable electrical charges (Positives and negatives)
They result from ionic substitutions of Si for Al or of Al for Mg or Fe(II) in the crystal structure	They result from reactions between H^+ and O^{2-} ions existing on the surface of mineral particles
Occurs only in 2:1 minerals and allophanes	Occurs in clay minerals 1:1, humus, and Fe and Al oxides
Not influenced by environmental conditions or pH dependent	They are influenced by the conditions of the environment and dependent on pH
Internal origin and are always negative	External origin and can be negative or positive

define the different mineral species and are responsible for many of their unique properties [50]. The structural schemes, physical and chemical characteristics and environmental importance of these minerals are discussed in the following items.

3 Major phyllosilicate Groups

The weathering of minerals and phyllosilicates releases nutrients to plants, which are retained by other minerals through adsorption, cation exchanges and precipitation [50]. Clay minerals are weathering indicators, as the presence or absence of specific minerals give clues about the genesis and dynamics of the environment, such as soil formation, dissolution, pollutant concentration, adsorption, absorption or dispersion of nutrients.

The physical and chemical characteristics of clay minerals are also important for urban planning, construction and maintenance of buildings, roads and airports. They are inputs for industry, in addition to being used to adsorb organic and inorganic environmental pollutants, attenuating their movement in the environment or preventing their absorption by plants [30, 50]. Knowing phyllosilicates, their influence on soils and interactions with fungi, bacteria and plants is essential for the creation of phytoremediation strategies and recovery of degraded areas [1, 2, 3, 4, 42, 47].

Schulze [50] points out that some minerals are pollutants themselves and can cause serious environmental problems when exposed to weathering. Therefore, understanding phyllosilicates is also often the key to solving environmental problems. Next, the main classes of phyllosilicates are presented, highlighting their physical, chemical, structural characteristics, genesis and environmental importance.

3.1 Kaolinite-Serpentine Group

The kaolinite-serpentine group is composed of two subgroups: (a) kaolinite subgroup—composed of dioctahedral minerals, mainly kaolinite and halloysite; (b) serpentine subgroup—composed of trioctahedral minerals, mainly chrysotile and antigorite (Table 1).

Kaolinite is a phyllosilicate formed by a sheet of siloxane (T) joined to a sheet of the type gibbsite (O), structure 1:1, it is presented in the form of plates due to the stacking one above the other of the sheets T-O. Kaolinite is dioctahedral and contains Al^{3+} at octahedral sites and Si^{4+} at tetrahedral sites (Fig. 3). The 1:1 layer is electrically neutral, and the adjacent layers are held together by hydrogen bonds between the basal oxygens of the tetrahedral sheet and the surface plane hydroxyls of the adjacent octahedral sheet [50].

Kaolinite has a basal spacing of 0.72 nm, chemical composition $Al_2Si_2O_5(OH)_4$, the specific surface area varies from 10 to 20 $m^2\ g^{-1}$, and the cation exchange capacity varies from 3 to 15 $cmol_c dm^{-3}$ (Table 3), being pH dependent because of the hydroxyls along the edges of the mineral. Depending on the H^+ or OH^- of the soil solution or the environment, hydroxyls can be protonated or deprotonated and give rise to positive or negative charges, reflecting, respectively, the anion exchange capacity or cation exchange capacity [40].

Kaolinite can form in soils from Al and Si released by the weathering of primary and other secondary minerals, such as feldspars from igneous rocks. In addition, it can be inherited from other soil source materials, such as sedimentary rocks. Kaolinites extracted from mineral deposits are widely used in industrial applications, such as fillers for plastics, ceramics and paper coatings [50].

The 1:1 layer has little or no permanent charge due to the low amount of substitution in the tetrahedral or octahedral sheets, and most kaolinites are close to ideal for the formula $Al_2Si_2O_5(OH)_4$. Therefore, exchange capacities and surface areas

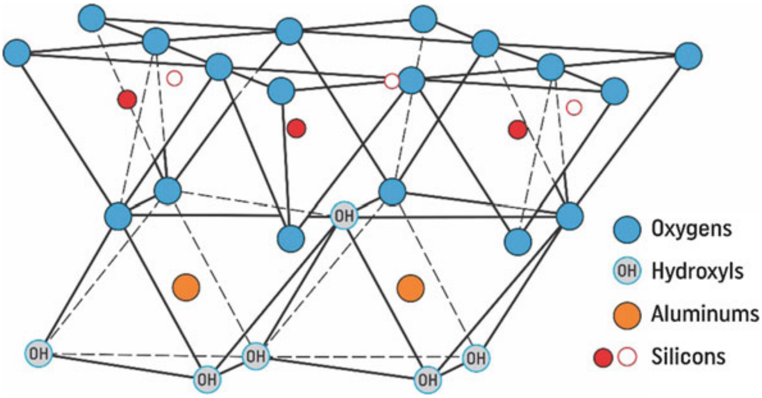


Fig. 3 Schematic of the structure of kaolinite. *Source* Adapted from [23, p. 46]

Table 3 Cation exchange capacity (CEC) and specific surface of materials (SS)

Phyllosilicates	CEC ($\mathrm{cmol_c dm^{-3}}$)	SS ($\mathrm{m^2\ g^{-1}}$)	References
Vermiculite	115–250	~800	[21, 38]
Smectite	50–160	600–800	[11, 48]
Chlorite	10–40	26–45	[30, 32]
Illite	5–15	*	[30, 58]
Palygorskite Sepiolite	5–30 20–45	~800–900	[55]
Kaolinite	3–15	10–20	[9, 23, 40, 50, 62]
Talc-pyrophyllite	~2	~10–43,7	[65]

*Information on illite specific surface (SS) is scarce and existing information is not consistent for soils

are low, giving soils low chemical fertility when compared to soils dominated by 2:1 clay. Kaolinite is a common mineral in soils, being normally abundant in highly weathered soils, such as Ultisols and Oxisols [50].

Kaolinites interfere with several physical and chemical processes in soils, such as aggregate formation, increased porosity, water retention, drainage, cation and anion exchange reactions, among others [40]. In hypoferric soils, kaolinites are associated with the formation of block structure and cohesive horizons present in soils developed from the Barreiras Formation, a geological unit found throughout the Brazilian coast [44].

The cohesive horizons developed in soils of the Barreiras Formation are dense subsurface horizons, which are hard when dry and friable when wet. This behavior is probably due to the transport of small kaolinites from the surface horizons of soils and subsurface precipitation, and the mechanisms involved in the process are detailed in the works of [17] and [44] (Fig. 4).

Halloysite has a similar crystallographic structure to kaolinite; however, the 1:1 sheets are separated by a layer of H2O molecules (Fig. 5) and generally

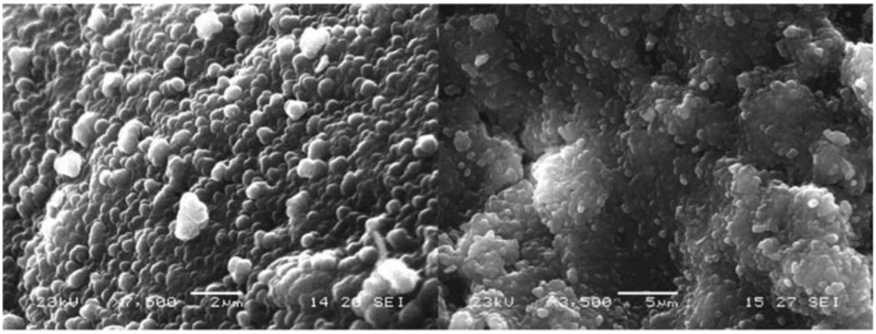


Fig. 4 SEM photomicrograph of kaolinite in a cohesive horizon

occur as tubular or spherical particles. Halloysite is usually found in soils formed from volcanic deposits (volcanic ash and obsidian) such as Andisols. Halloysite is formed at the beginning of the weathering process, being less stable than kaolinite, transforming into it over time [50].

The phyllosilicates of the kaolinite subgroup perform important environmental functions, as summarized in Table 4 in final considerations. In soils, they are responsible for several physical and chemical processes that interfere, for example, in the formation of aggregates, especially subangular ones, and in the increase in porosity, they are responsible for retaining anions at acidic pH and cations at high pH and have the possibility of retaining nitrates at acidic pH.

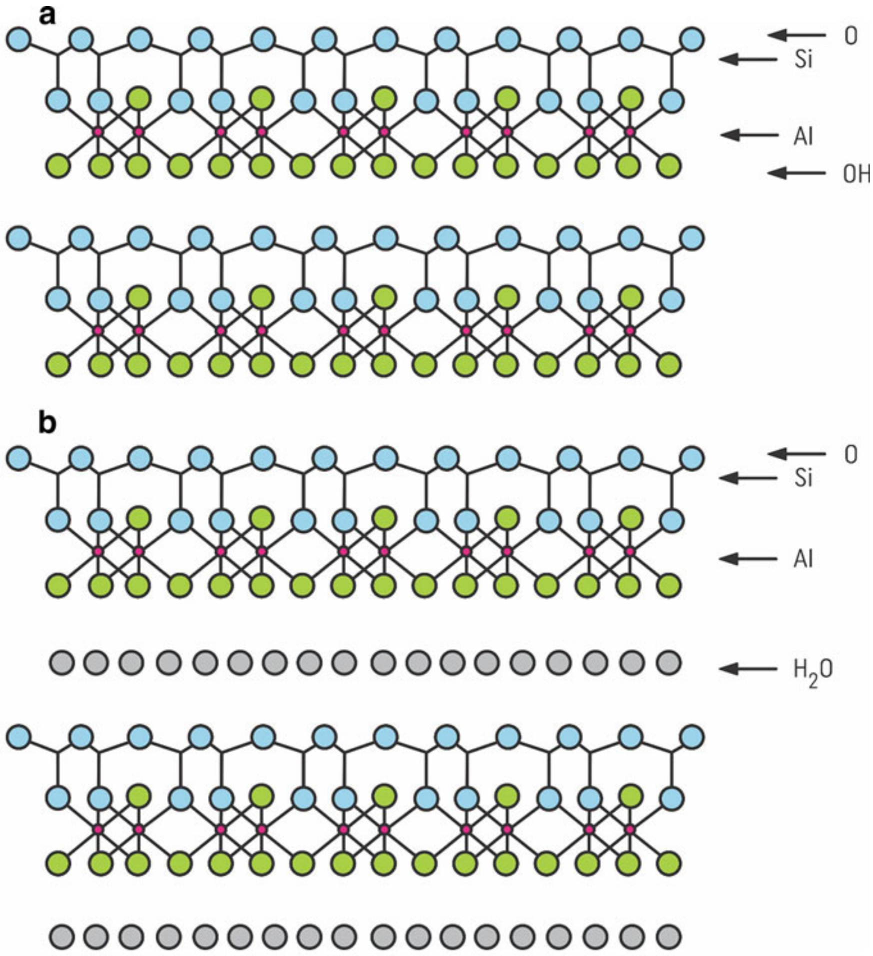


Fig. 5 Schematic of the structure of kaolinite and halloysite. *Source* Adapted from [51]

Table 4 Environmental importance of phyllosilicates

Phyllosilicates	Environmental importance	References
kaolinite and halloysite	Retention of anions at acidic pH and cations at high pH; possibility of retention of nitrates in acidic pH; greater physical stability, less plasticity, greater water retention capacity, confers less erodibility to the soil, low expansion/contraction capacity, less dispersibility, weak sorption and less metals when compared to phyllosilicates 2:1, when associated with iron oxides can favor the sorption of metals and anions, can be used to adsorb radionuclides, such as Cs and Ra, as well as oil residues from oil extraction, spills and other disasters in the marine environment; can be used to mitigate problems related to hazardous organic pollutants even in small concentrations, such as phenols; they have a lower ability to buffer acidification when compared to smectites, the interaction between kaolinite, iron oxides and organic matter (SOM) favors a decrease in the rate of SOM decomposition, favors the adsorption of organic molecules; are good environmental indicators, especially in more weathered environments	[8, 12, 16, 19, 27, 29–31, 37, 50, 56, 60, 62]
Serpentine	As they are formed from the weathering of ultramafic rocks, their presence together with the predominance of magnesium in the exchange sites can hinder calcium adsorption and plant development, as well as concentrate high levels of heavy metals	[30, 62]

(continued)

Table 4 (continued)

Phyllosilicates	Environmental importance	References
Talc and pyrophyllite	They are sources of potassium (K), non-expandable, soft and have poor cohesion. They are rare in soils, but when present they indicate that the soil is poorly weathered. They are soft, foliated morphology, inertia, purity, whiteness, high melting point, high thermal conductivity and low electrical conductivity and low chemical reactivity	[30, 50, 65]
Mica	Most common sources of potassium (K) in soils; its alteration can generate vermiculite, smectite and interstratified, which are also macronutrient reserves; can be used to adsorb radionuclides, such as Cs and Ra, as well as oil residues from oil extraction, spills and other disasters in the marine environment	[30, 35, 41, 50, 54, 58]
Vermiculite	Increases the cation exchange capacity of the soil; adsorbs radionuclides and heavy metals, such as Cs, Ra and Cu; selectively adsorbs cations preferentially K^+, $NH_4{}^+$, Rb^+ and Cs^+; favors cationic exchange of ions that have high hydration energy, such as Ca^{+2} and Mg^{+2}	[30, 38]
Smectite	They confer high fertility to the soils; organic compounds adsorption, herbicides and pesticides; enhanced anionic polymer adsorption; it has a high potassium (K) fixation potential; high potential for fixing toxic elements, such as heavy metals; are very useful in waste dumps when used properly, especially due to their high expansion pressure, low hydraulic conductivity and high CEC	[18, 30, 33, 34, 48, 50, 53, 57]

(continued)

Table 4 (continued)

Phyllosilicates	Environmental importance	References
Chlorite	It is capable of adsorbing heavy metals and radioactive elements such as Cr and Cs; has selectivity for cations with low hydration energies, such as K^+, $NH_4{}^+$ e Rb^+	[32]
Sepiolite-Palygorskite	Used as gelling agents to keep other solids in suspension; in oil well drilling; in asphalt-based coatings, sealing and paving; in the handling and distribution of liquid fertilizers; as oil adsorbents; for pharmaceutical purposes; as supports for biocides; for absorption and adsorption of animal waste; to cover the floor of herd-carrying wagons	[30, 55]

The phyllosilicates of the kaolinite subgroup provide greater physical stability, less plasticity, greater water retention capacity and less soil erodibility. They have low expansion/contraction capacity, lower dispersibility, weak sorption and lower capacity to buffer acidification when compared to 2:1 phyllosilicates, such as smectite. When associated with iron oxides, kaolinitic minerals can favor the sorption of metals and anions; in addition, it can favor the reduction of the decomposition rate of organic matter.

Minerals from the kaolinite family are good indicators of hot and humid environments, especially kaolinite. In addition, they can be:

(a) used in the recovery of degraded areas and/or contaminated by heavy metals and organic compounds [16, 22, 29, 37, 60],
(b) in the adsorption of oil residues from oil extraction, spills and other disasters in the marine environment [6, 19, 56] and,
(c) as physical and chemical barriers against emerging pollutants such as microplastics (MPs), already commonly identified in the atmosphere, lakes, rivers, seas, glaciers, living beings and in the soil-groundwater system.

As phyllosilicates are important components of the soil-groundwater system, [63] performed an experiment on the mobilization of MPs, notably polystyrene nanoparticles in quartz sand mixed with kaolinite, montmorillonite and illite on the mobility of MPs in groundwater and suggest that kaolinite has a greater effect on inhibiting the mobility of MPs, but montmorillonite and illite also play this role. This is because the change in ionic strength can change the surface charge of MPs and clay minerals, affecting the interaction energy. The findings of [63] can help to understand the transport mechanisms of microplastics in porous media and provide subsidies to simulate microplastic contamination in groundwater.

In recent decades, many hazardous and toxic organic pollutants have been detected in soils, surface waters, groundwater and even drinking water, arising from conventional or emerging activities and products, such as additives incorporated into MPs. Additives are chemical products that have heavy metals added to the plastic to color, provide transparency, improve mechanical, thermal and electrical resistance and degradation by ozone, light radiation, mold, bacteria and moisture and include inert or reinforcing fillers, plasticizers, antioxidants, ultraviolet light stabilizers, lubricants, dyes and flame retardants [26]. Such additives and the degradation of organic compounds that make up MPs can pose a threat to human health, some of them even in low concentrations, such as phenolics.

Phenolics are chemicals that pose a threat to human health even in low concentrations and can enter the human body through the skin or esophagus and cause damage to the protein structure of our body [7, 36, 66].

According to Senthilvelan et al. [52], 700 million tons of phenol are produced annually as a raw material in the petroleum and chemical industries. That's why we need to develop technologies for the efficient treatment of wastewater to protect ourselves. Wang et al. [60] developed a new low-cost carbon catalyst that is efficient in removing phenol from the carbonization of halloysite at different temperatures (600, 700, 800 and 900 °C), showing the importance of this group of phyllosilicates in the environmental area.

The abundance, geochemical stability and physical and chemical characteristics of clay minerals from the kaolinite family favor their use in the biogeoengineering industry applied to environmental management, which includes the development and application of techniques for area recovery and contaminant control, as well as such as monitoring environmental resources such as soil and water.

The serpentine subgroup consists of 1:1 trioctahedral phyllosilicates, similar in structure to kaolinite but containing a variety of cations in the octahedral sheet, such as Fe II, Fe III, aluminum, magnesium, manganese, nickel and zinc. Serpentine normally occurs in large grains, but appears as small plaques and fibrous structures, as is the case with chrysotile, widely used in the past as a constituent of asbestos, a carcinogenic material [62].

The serpentine subgroup minerals do not have a significant permanent charge, so it is inferred that the cation exchange capacity is mainly due to the variable charge at the edges of the crystals and the values are similar to those of kaolinite.

The serpentines are formed from the weathering of ultramafic rocks, so it can favor the concentration of heavy metals in the soil. The presence of minerals from this subgroup has a predominance of magnesium in the exchange sites, which hinders calcium absorption and impairs plant development. They are indicators of poorly weathered soils and have several environmentally unfavorable characteristics, such as occurrence in shallow soils that are more prone to erosion [30, 62].

3.2 Talc and Pyrophyllite

The talc-pyrophyllite group is composed of two subgroups: (a) talc subgroup—composed of trioctahedral minerals, mainly talc; (b) pyrophyllite subgroup—composed of dioctahedral minerals, mainly pyrophyllite (Table 1). The simple structures of talc and pyrophyllite are good starting points for discussing the structures of 2:1 phyllosilicates (Fig. 6).

Talc and pyrophyllite consist of 2:1 layers stacked on top of each other, with the former having Mg^{2+} at the octahedral sites and the latter having Al^{3+} at the octahedral sites. The tetrahedral sheets of both minerals have only Si^{4+}, the talc formula being $Mg_3Si_4O_{10}(OH)_2$ and from pyrophyllite $Al_2Si_4O_{10}(OH)_2$ [50]. In both subgroups, the charges are balanced within the 2:1 layer, making them electrically neutral. Adjacent 2:1 layers are held together by weak van der Waals forces, which can be easily separated, which explains their tendency for prominent basal cleavage, high softness, and low hardness (from 1 to 2) on the Mohs scale.

They have a basal spacing of 0.92–1.0 nm, specific surface area of ~10 to 43.7 $m^2\ g^{-1}$ and very low cation exchange capacity (~2$cmol_c dm^{-3}$) (Table 3). Only the edges of the layers provide potentially reactive sites, which are pH dependent and also influenced by particle size. The ions (cations and anions) that bind to the edges of talc-pyrophyllite probably do so through a specific adsorption (chemisorption) or inner sphere binding mechanism [65].

Talc and pyrophyllite are used industrially as ingredients in paints, ceramics, plastics, papers and cosmetics, so when they are found in river and estuarine environments, they are indicators of industrial activity, if there is no proximal geological source [50].

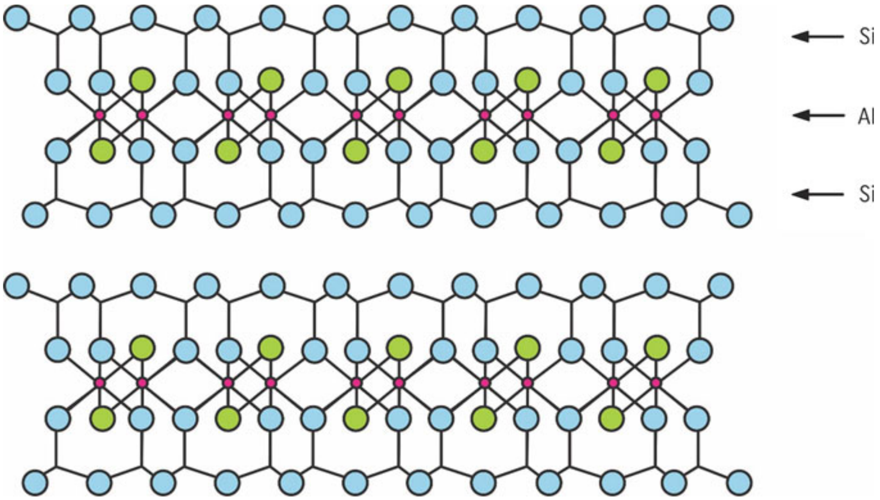


Fig. 6 Schematic of the structure of talc-pyrophyllite. *Source* Adapted from [51]

The most important physical and chemical characteristics of talc-pyrophyllite are softness, foliated morphology, inertia, purity, whiteness, high melting point, high thermal conductivity, low electrical conductivity and low chemical reactivity, because they are practically electronically neutral [65]. They are non-expansive sources of potassium (K), rare in soils, but when present, they indicate that the soil is poorly weathered [30].

3.3 Mica

The mica group is composed of two subgroups, one composed of trioctahedral minerals, mainly represented by biotite and phlogopite, and the other composed of dioctahedral minerals, represented by muscovite and illite (Table 1). Mica have the 2:1 layer structure described for talc and pyrophyllite (Figs. 7, 8 and 9), but with two important differences, according to [50]:

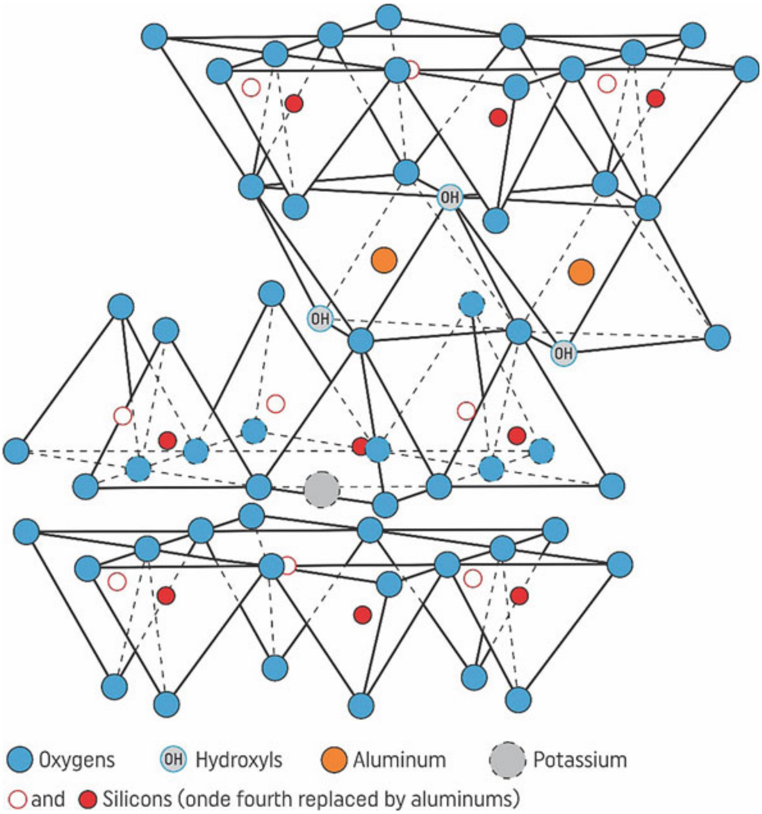


Fig. 7 Schematic of the structure of muscovite. *Source* Adapted from [23], p. 66

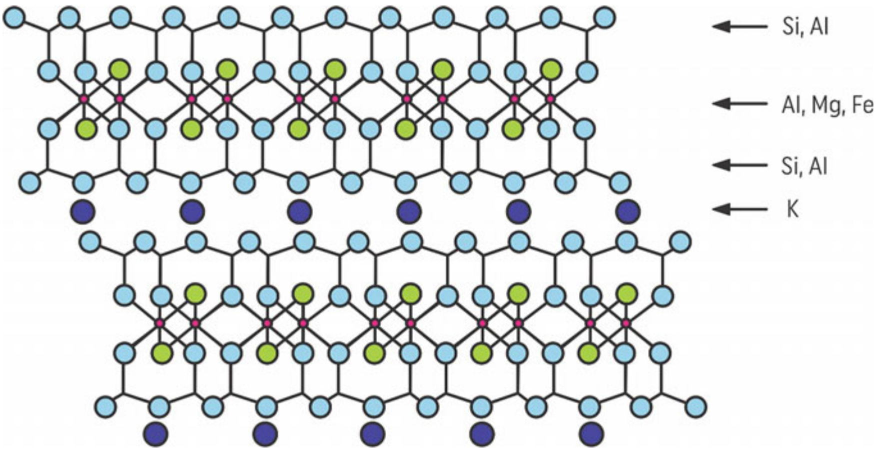


Fig. 8 Structural scheme of dioctahedral mica. *Source* Adapted from [51]

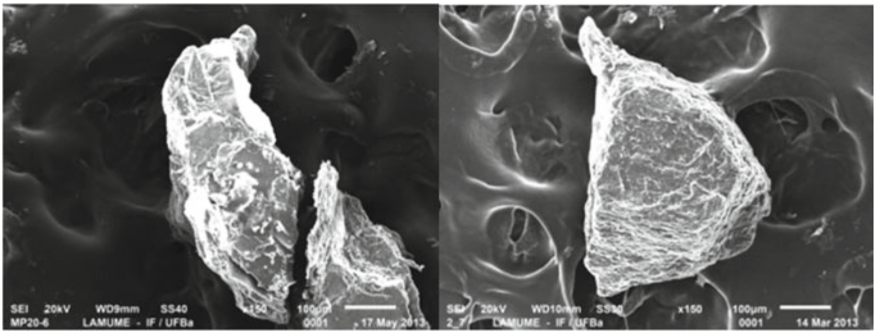


Fig. 9 Photomicrograph of biotite. Images kindly provided by Gileno Moreira dos Santos

(a) instead of having only Si^{4+} at the tetrahedral sites, a quarter of the tetrahedral sites are occupied by Al^{3+}. Because of this substitution, there is an excess of one negative charge per formula unit in the 2:1 layer;

(b) excess negative charge is commonly balanced by K^+, which occupy intermediate sites between two 2:1 layers. Therefore, the ideal formula for a mica mineral with Al at the octahedral sites is $KAl_2(AlSi_3)O_{10}(OH)_2$.

Mica can be dioctahedral or trioctahedral, because Fe^{2+} and Fe^{3+} can replace Mg^{2+} and Al^{3+} in the octahedral sheet and Na^+ and Ca^{2+} can replace K^+ in the middle layer [58]. Mica in soils is inherited from the parent rock, usually those derived from igneous or metamorphic rocks or from sediments derived from these rocks.

Muscovite, biotite and phlogopite are the most common minerals, and all have K^+ in the middle layer; however, they differ in the composition of the octahedral sheet and whether they are di- or trioctahedral [50]. In soils, the most common micas are muscovite and illite, because the dioctahedral ones are more resistant to weathering.

Mica has a basal spacing of the layer+interlayer (structural unit) of 1.0 nm, high specific surface area (between 65 and 100 m^2 g^{-1}) and low cation exchange capacity of the clay fraction (illite), between 5 and 15 $cmol_c dm^{-3}$ (Table 3). Values of up to 40 $cmol_c dm^{-3}$ reported for illite and glauconite in the literature are due to inter-bedding, mainly of illite-smectite [30].

Mica are environmentally significant because they are the most common sources of potassium (K) in soils, in addition to being sources of Fe (II) and because they facilitate the fixation of weakly hydrated cations, such as NH_4^+, Rb^+ and radionuclides such as Cs^+ [58]. Mica weathering can generate vermiculite and smectite. When present in soils, they may indicate that they are poorly weathered. Micaceous minerals, such as illite, can also be used to inhibit the mobility of MPs [63].

3.4 Vermiculite

The vermiculite group is composed of two subgroups, one trioctahedral and the other dioctahedral (Table 1). Vermiculite has a similar 2:1 layer structure to mica, but instead of having a layer charge of ~1 per formula unit and K^+ at interlayer positions, it has a layer charge of 0.9–0.6 and contains cations, mainly Ca^{+2} and Mg^{+2}, in the middle layer (Fig. 10) [38].

It has the ability to expand in water like smectite, but not as extensively because of the presence of only two planes of water molecules surrounding the hydrated cations in the interlayer space. It has the following ideal formulas: (a) trioctahedral vermiculite: $[nH_2O, Mg_x(Mg_3) (Si_{4-x}Al_x)O_{10}(OH)_2]$—originated from the transformation of biotite; (b) dioctahedral vermiculite: $[nH_2O, Mg_x(Al_2) (Si_{4-x}Al_x)O_{10}(OH)_2]$—originated from the transformation of muscovite [30].

The high charge per formula unit gives vermiculite a high cation exchange capacity (CEC), ranging from 115 to 250 $cmol_c dm^{-3}$ [21] and the specific surface around ~800m^2 g^{-1} [38]. They have the ability to selectively adsorb cations with low hydration energy, such as K^+, NH_4^+, Rb^+ e Cs^+. In addition, it favors cationic exchange of ions that have high hydration energy, such as Ca^{+2} e Mg^{+2}.

Vermiculite in soils is believed to form almost exclusively from the weathering of micas and chlorites. The weathering of micas to vermiculite (or smectite) probably occurs by substitution of K^+ at the interlayer sites by hydrated exchangeable cations. The integrity of the 2:1 layer is preserved, but there is a reduction in layer load [50].

Vermiculite plays an important role in regulating nutrient dynamics for plants, sometimes even acting as a source or sink for various elements. Due to its high cation exchange capacity (CEC) together with the ability to fix certain ions, it is suitable for removing contaminants, including heavy metals, radionuclides and grounded nuclear waste [20, 38, 59].

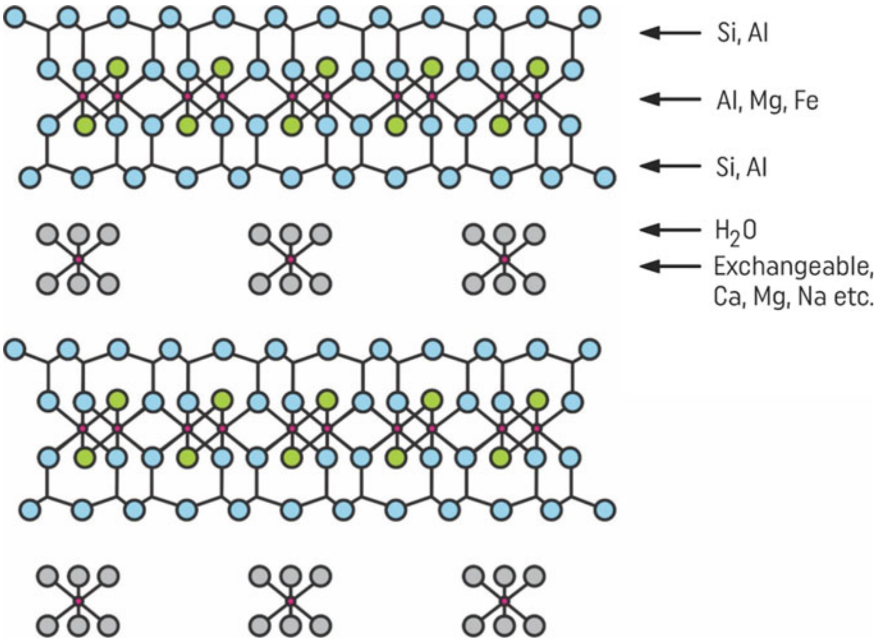


Fig. 10 Schematic of dioctahedral vermiculite and smectite structural units with interlayer hydrated cations. *Source* Adapted from [51]

Its ability to expand and exfoliate at high temperatures makes it useful in many industrial applications such as horticultural potting media, thermal insulation materials, soil conditioners and substrates [38, 50].

3.5 Smectite

The smectite group is composed of two subgroups, one composed of trioctahedral minerals, mainly represented by saponite, hectorite and sauconite, and the other composed of dioctahedral minerals, represented by montmorillonite and beidellite (Table 1). The smectite group consists of 2:1 minerals (Fig. 11), with an intermediate layer containing exchangeable cations and a charge ranging from 0.6 to 0.25.

Dioctahedral smectites are more common in soils than trioctahedral ones, the main representatives being montmorillonite, beidellite and nontronite, which differ in tetrahedral composition and in octahedral sheets [48]. Smectites do not fix K^+ as readily as vermiculite because they have a lower layer charge; however, they are more expansive [50].

Smectites contract when dry and expand when wet, leading to cracking and displacement problems when houses, roads and other structures are built on smectitic

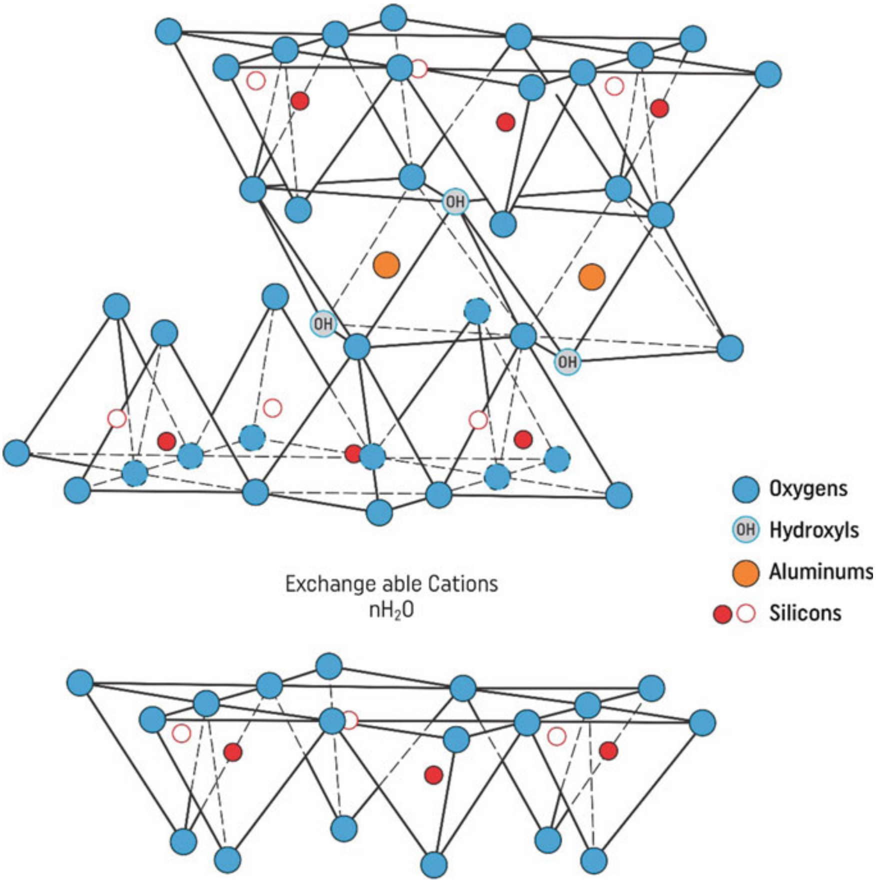


Fig. 11 Schematic of the structure of montmorillonite. *Source* Adapted from [23], p. 56

soils such as Vertisols [50]. As the expansive capacity of 2:1 minerals and the intensity of this expansion are related to the charge of the layer and its tetrahedral or octahedral origin, this explains why montmorillonite is more expansive than beidellite, as it has an isomorphic octahedral substitution.

Due to high specific surface area (600 a 800 $m^2 g^{-1}$), its adsorptive properties and high cation exchange capacity (47 a 162 $cmol_c dm^{-3}$) (Table 3), smectites are used as catalysts, adsorbents for spills of liquid substances and oils, as sealants for ponds and wells, in drilling fluids for oil wells and in landfill linings [50].

The smectite group has important implications for agriculture, engineering and environmental purposes, as they are expansive, the specific surface area and the cation exchange capacity are high [48]. Therefore, they provide good soil fertility, are good reservoirs of macronutrients, adsorb organic compounds, herbicides, pesticides, have a high potential for fixing potassium (K) and a high potential for fixing toxic elements, such as heavy metals.

The high expansiveness of the smectite group, especially montmorillonite, can hinder agricultural uses and management and their use as borrowing materials for the construction of roads, buildings and houses, for example. They can present geotechnical risks, such as cracks and ruptures in engineering works; however, they are very useful in waste deposits when used properly, especially due to their high expansion pressure, low hydraulic conductivity and high CEC.

Recent research also points out that smectites can be used to inhibit the mobility of emerging contaminants, such as PMs and contaminants associated with them [63].

3.6 Chlorite

The chlorite group is composed of two subgroups, one composed of trioctahedral minerals, mainly represented by clinochlore, and the other composed of dioctahedral minerals, represented by donbassite (Table 1).

Chlorite has a 2:1 layer structure with excess negative electrical charge, the excess charge being balanced by a positively charged interlayer hydroxide sheet [32] (Fig. 12). Any octahedral sheet, whether part of the 2:1 layer or the hydroxide interlayer, can be di- or trioctahedral and contain Mg^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Al^{3+}, Fe^{3+} e Cr^{3+}, giving rise to different types of minerals [50].

The union between the 2:1 layer and the hydroxide layer occurs through hydrogen bonding, resulting in a fixed basal spacing of 1.4 nm. As they do not expand, they have a low specific surface (26–45 $m^2\ g^{-1}$) [32] and the cation exchange capacity between 10 and 40$cmol_c dm^{-3}$ (Table 3) [30]. Part of the CEC is pH dependent and is associated with $Al(OH)_3$ groups at the edge of the minerals. Chlorite group minerals are rare in soils, and when they occur, they are inherited from metamorphic rocks, igneous rocks or hydrothermally altered sediments. Chlorite group minerals transform into vermiculite and smectite and are sensitive to chemical weathering [50].

Chlorite has aroused environmental interest because it is capable of adsorbing heavy metals and radioactive element ions, such as chromium and cesium. In addition, it has selectivity for cations of low hydration energies, such as K^+, NH_4^+ e Rb^+, and can adsorb anions at the exposed edges of the mineral, because they generate pH-dependent charges.

3.7 Sepiolite and Palygorskite

The sepiolite-palygorskite group is composed of two subgroups, the sepiolite, which is trioctahedral, and the palygorskite, which is dioctahedral (Table 1). Sepiolite and palygorskite minerals are considered phyllosilicates, but are structurally distinct from typical 1:1 and 2:1 layer structures in that they have continuous tetrahedral sheets, but with adjacent bands of tetrahedra within a tetrahedral sheet that point in two

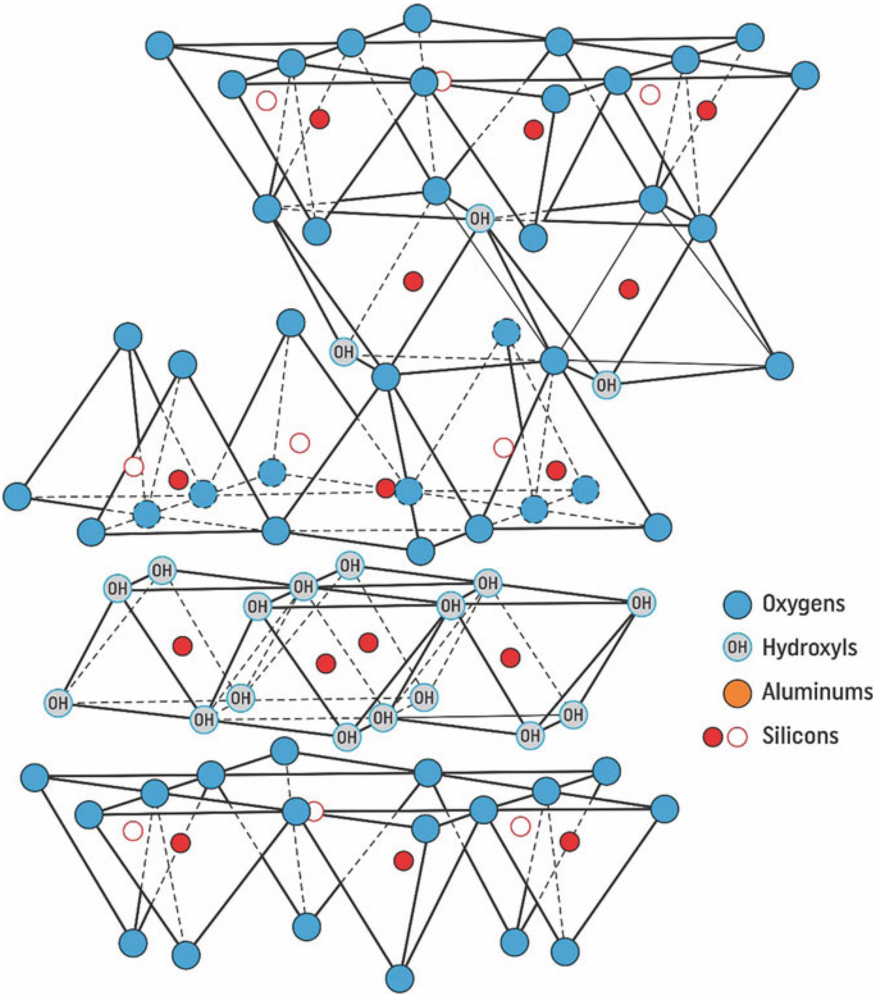


Fig. 12 Schematic of the structure of chlorite. *Source* Adapted from [23], p. 70

opposite directions. Water molecules occur in the spaces between the leaves, with the 2:1 leaves being wider in sepiolite than in palygorskite [50].

Sepiolite is a low aluminum trioctahedral magnesium silicate with ideal formula $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4.8H_2O$, while palygorskite is intermediate between di- and trioctahedral, with ideal formula $Si_8Mg_5O_{20}(OH)_2(OH_2)_4.4H_2O$ [55], and having equal proportions of Al and Mg [30]. Minerals have low CEC, ranging from 5 to 30 $cmol_ckg^{-1}$ to the palygorskite and from 20 to 45 $cmol_ckg^{-1}$ to the sepiolite [55],both have high specific surface (Table 3).

They are mostly found in soils in arid and semi-arid environments, have a fibrous morphology and apparently consist of aggregates or bundles of thin laths, oriented in parallel and with a width of 10–35 nm and a thickness of 5–10 nm [55]. Due to their fibrous morphology, the suspension of these clays can form thick gels even at low concentrations of solids. Therefore, they are used industrially as gelling agents to keep other solids in suspension [50].

Sepiolite and palygorskite can also be used as thixotropic agents in oil well drilling in saline regions, for asphalt-based coatings, sealing and paving, in the handling and distribution of liquid fertilizers, as oil adsorbents, and for pharmaceutical purposes, as substrate primers for biocides, for absorption and adsorption of animal excrement and for covering the floor of cattle transport wagons.

4 Final Considerations

The physical and chemical characteristics of phyllosilicates play important roles in the dynamics of the environment, as expressed throughout the chapter. The knowledge of such properties can favor their use to stop or mitigate the contamination of degraded areas by different types of substances, whether organic, mineral or radioactive. A summary of the environmental importance of phyllosilicates is presented in Table 4.

The table summarizes the importance of phyllosilicates in environmental management and, in a way, signals the importance of expanding research to improve the techniques that use them as absorbing and adsorbing agents for contaminants. New horizons are approaching, signaling the importance of deepening knowledge about phyllosilicates and other clay minerals as actors to safeguard the environment.

Acknowledgements In Memoriam, to professors Ilson Guimarães Carvalho, Lucedino Paixão Ribeiro and Tersandro Paz do Rego Monteiro, Brazilian geoscientists who taught so much about clay minerals and their environmental importance. The authors thank Leandro Fonseca Carvalho and biologist Mr. Jackson M. Ministro for his help with figures. The authors also thank Prof. MSc. Gileno Santos Moreira for kindly providing photomicrographs of the biotite.

References

1. Alves, L.J., et al.: Uranium transfer in grasses grown on mining waste and natural soil. J. Environ. Radioact. **251–252**, 106973 (2022)
2. Alves, L.J., et al.: Microbial approach for alleviation of potentially toxic elements in agricultural soils. In: Prasad, M.N.V., Pietrzykowski, M. (Eds.) Climate Change and Soil Interactions: Managing Soil System for Environmental Sustainability, 1st edn, vol. 1, pp. 271–303. Elsevier, Amsterdã (2020)
3. Alves, L.J., et al.: Uranium mine waste phytostabilization with native plants—a case study from Brazil. In: Prasad, M.N.V., de Campos Favas, P.J., Maiti, S.K. (Eds.) Bio-Geotechnologies for Mine Site Rehabilitation, 1st edn, vol. 1, pp. 299–322. Elsevier, Amsterdã (2018)
4. Alves, L.A.: Micorriza arbuscular como ferramenta biotecnológica para controle da transferência de urânio. Tese de doutorado. UESC (2018), 193p.

5. Bailey, S.W. (Ed.): Hydrous phyllosilicates (exclusive of micas). Mineralogical Society of America, Washington (1988) (Revi. Miner., 19)
6. Bantignies, J., Moulin, C.C., Dexpert, H.: Asphaltene adsorption on kaolinite characterized by infrared and Xray absorption spectroscopies. J. Petrol. Sci. Eng. **20**, 233–237 (1998)
7. Barrios-Estrada, C., Rostro-Alanis, M.J., Muñoz-Gutiérrez, B.D., et al.: Emergent contaminants: Endocrine disruptors and their laccase-assisted degradation—A review. Sci. Total Environ. **612**(15), 1516–1531 (2018). https://doi.org/10.1016/j.scitotenv.2017.09.013
8. Bayer, C., Martin-Neto, L., Mielniczuk, J., Pillon, C.N., Sangoi, L.: Changes in soil organic matter fractions under subtropical no-till cropping systems. Soil Sci. Soc. Am. J. **65**(5), 1473–1478 (2001). https://doi.org/10.2136/sssaj2001.6551473x
9. Besoain, E.: Mineralogia de arcillas de suelos. IICA, San José, 1216 p. (1985) (IICA/Série libros y materiales educativos, n. 60)
10. Bish, D.L.: Refinamento Rietveld da estrutura de caulinita a 1,5 K Clays Clay Miner, 41, pp. 738–744 (1993). https://doi.org/10.1346/CCMN.1993.0410613
11. Borchardt, G.A.: Smectites, pp. 675–727. In: Dixon, J.B., Weed, S.B. (Eds.) Minerals in Soil Environments, 2nd edn. SSSA Book Ser. 1. SSSA, Madison, WI (1989)
12. Braggs, B., Fornasiero, D., Ralston, J., et al.: The effect of surface modification by an organosilane on the electrochemical properties of kaolinite. Clays Clay Miner. **42**, 123–136 (1994). https://doi.org/10.1346/CCMN.1994.0420203
13. Brindley, G.W., Brown, G.: Crystal Structures of Clay Minerals and Their X-Ray Identification, p. 495p. Mineralogical Society, London (1984)
14. Brindley, G.W., et al.: Relation between structural disorder and other characteristics of kaolinites and dickites. Clays Clay Miner. **34**(3), 239–249 (1986)
15. Calderano, S.B. et al.: Análise mineralógica das frações finas do solo por difratometria de raios-X: revisão e atualização da metodologia e critérios usados na Embrapa Solos. Embrapa Solos, Rio de Janeiro (2009). (Embrapa Solos, Comunicado Técnico, 53)
16. Carbonell, V.V.R., et al.: Clay mineral assemblages as indicators of paleoenvironmental and diagenetic dynamics in the Neogene Fiambal´a Basin, NW Argentina. J. S. Am. Earth Sci. **118**(2022), 103949 (2022). https://doi.org/10.1016/j.jsames.2022.103949
17. Corrêa, M.M., et al.: Caracterização física, química, mineralógica e micromorfológica de horizontes coesos e fragipãs de solos vermelhos e amarelos do ambiente tabuleiros costeiros. R. Bras. Ci. Solo **32**, 297–313 (2008). https://doi.org/10.1590/S0100-06832008000100028
18. Coulombe, C.E., Wilding, L.P., Dixon, J.B.: Overview of vertissols: characteristics and impacts of society. Adv. Agron. **57**, 289–375 (1996). https://doi.org/10.1016/S0065-2113(08)60927-X
19. Dudášová, D., et al.: Estudo da adsorção de asfaltenos em diferentes minerais e argilas. Parte 1. Adsorção experimental com detecção de depleção de UV Colloids Surf, A **317**, 1– (2008). https://doi.org/10.1016/j.colsurfa.2007.09.023
20. Das, N.C., Bandyopadhay, M.: Removal of copper (II) using vermiculite. Water Environ. Res. **64**, 852–857 (1992)
21. Douglas, L.A.: Vermiculites. In: Dixon, J.B., Weed, S.B. (eds.) Minerals in Soil Environments, pp. 635–674. Soil Science Society of America, Madison (1989)
22. Formentini, T.A., Basile-Doelsch, I., Legros, S., et al.: Instability of OW-borne Cu(I) sulfide and role of clay and iron oxide minerals. Sci. Total Environ. **848**(20), 157779 (2022). https://doi.org/10.1016/j.scitotenv.2022.157779
23. Grim, R.: Clay mineralogy. McGrall-Hill Book Company (1953), 384p.
24. Gruner, J.W.: The Crystal Structure of Kaolinite. Zeitschrift für Kristallographie. Crystall. Mater. **83**(1) (1932). https://doi.org/10.1524/zkri.1932.83.1.75
25. Guggenheim, S., Martin, R.T.: Definition of clay and clay minerals: joint report of the AIPEA and CMS nomenclature committees. Clay Miner. **30**, 257–259 (1995)
26. Guo, J.J., et al.: Source, migration and toxicology of microplastics in soil. Environ. Int. **137**, 105263 (2020). https://doi.org/10.1016/j.envint.2019.105263
27. Jackson, T.A.: The biogeochemical and ecological significance of interactions between colloidal minerals and trace elements. In: Parker, A., Rae, J.E. (Eds.) Environmental Interactions of Clays. Springer, Berlin, Heidelberg (1998). https://doi.org/10.1007/978-3-662-03651-8_5

28. Johnston, C.T., Tombácz, E.: Surface chemistry of soils minerals. In: Dixon, J.B., Schulze, D.G. (Eds.) Soil Mineralogy with Environmental Applications, vol. 7, pp. 37–67. Soil Science Society of America, 677 South Segoe Road, Madison, WI 53711, USA. SSSA Book Series (2002)
29. Johnson, E.R., Otero-De-La-Roza, A.: Adsorption of organic molecules on kaolinite from the exchange-hole dipole moment dispersion model. J. Chem. Theory Comput. **8**(2012), 5124–5131 (2012). https://doi.org/10.1021/ct3006375
30. Kampf, N., Curi, N.: Argilominerais em solos brasileiros. In: Tópicos em Ciência do Solo. pp. 1–54. SBCS (2003)
31. Kazem, M.S., Abbas, A.M.: Study of inorganic doping of kaolin clay, a kinetic study of adsorption of methyl green dye from its aqueous solutions. Eurasian Chem. Commun. **4**, 1218–1227 (2022). https://doi.org/10.22034/ecc.2022.342243.1467
32. Kohut, C.K., Warren, C.J.: Chlorites. Soil Science Society of America, 677 South Segoe Road, Madison, WI 53711, USA. Soil Mineralogy with Environmental Applications, vol. 7, pp. 531–553. SSSA Book Series (2002)
33. Laird, D.A., Sawhney, B.L.: Reactions of pesticides with soil minerals. In: Dixon, J.B., Schulze, D.G. (Eds.) Soil Mineralogy with Environmental Applications, pp. 765–793. Madison, Soil Science Society of America (2002). https://doi.org/10.2136/sssabookser7.c26
34. Lee, J.F., et al.: Shape-selective adsorption of aromatic molecules from water by tetramethylammonium–smectite. J. Chem. Soc. Faraday Trans. 1F **85**, 2953–2962 (1989).
35. Long, J., et al.: Adhesion of single polyelectrolyte molecules on silica, mica, and bitumen surfaces. Langmuir **22**, 1652–1659 (2006). https://doi.org/10.1021/la052757f
36. Li, J., Zhang, B., Liu, M., Wang, Y.: Numerical simulation of the large-scale malignant environmental pollution incident. Process Saf. Environ. Protect. **87**, 232–244 (2009)
37. Li, C., et al.: Efficient catalytic degradation of bisphenol A coordinated with peroxymonosulfate via anchoring monodispersed zero-valent iron on natural kaolinite. Chem. Eng. J. **448**(2022), 137746 (2022). https://doi.org/10.1016/j.cej.2022.137746
38. Malla, P.B.: Vermiculites. Soil Science Society of America, 677 South Segoe Road, Madison, WI 53711, USA. Soil Mineralogy with Environmental Applications, vol. 7, pp. 501–529. SSSA Book Series
39. McBride, M.B.: Environmental Chemistry of Soil, p. 406p. Oxford University Press, New York (1994)
40. Melo, V.F., Wypych, F.: Caulinite e haloisita. In: Química e Mineralogia do Solo, Parte I (Eds. Vander de Freitas Melo & Luís Reynaldo Ferracciú Alleoni). 695p. pp. 427–504 (2009)
41. Natarajan, A., et al.: Understanding mechanisms of asphaltene adsorption from organic solvent on mica. Langmuir **30**, 9370–9377 (2014). https://doi.org/10.1021/la500864h
42. Nunes, F.C., et al.: Phytoremediation strategies for rehabilitation of soils affected by red mud: the Mariana Tailing Dam Collapse (Minas Gerais Brazil. Eur. Soil Sci. **1**, 1–13 (2022)
43. Nunes, F.C., et al.: Ecological engineering and ecosystem services—theory and practice. In: Prasad, M.N.V. (Ed.) Handbook of Ecological and Ecosytem EngIneering, 1st edn, vol. 1, pp. 1–24. John Wiley & Sons (2021)
44. Nunes, F.C., et al.: Soil as a complex ecological system for meeting food and nutritional security. In: Prasad, M.N.V., Pietrzykowski, M. (Eds.) Climate Change and Soil Interaction, 1st edn, vol. 1, pp. 22–269. Elsevier, Amsterdã (2020)
45. Nunes, F.C., et al.: Solos vermelhos e amarelos coesos de tabuleiros costeiros: gênese, evolução e influência da neotectônica. Caminhos da Geografia (UFU. Online), vol. 20, pp. 294–314 (2020). https://doi.org/10.14393/RCG207241145
46. Pauling, L.: The structure of the chlorites. Proc. Natl. Acad. Sci. USA **16**(9), 578–582 (1930). https://doi.org/10.1073/pnas.16.9.578.PMID:16587609;PMCID:PMC526695
47. Prasad, M.N., et al.: Global remediation industry and trends. In: Prasad, M.N.V. (Ed.) Handbook of Assisted and Amendment-Enhanced Sustainable Remediation Technology, 1st edn, vol. 1, pp. 3–28. John Wiley & Sons (2021)
48. Reid-Soukup, D.A., Ulery, A.L.: Smectites. Soil science society of America, 677 South Segoe Road, Madison, WI 53711, USA. Soil Mineralogy with Environmental Applications, vol. 7, pp. 467–499. SSSA Book Series (2002)

49. Sato, T., Watanabe, T., Otsuka, R.: Effects of layer charge, charge location, and energy change on expansion properties of dioctahedral smectites. Clays Clay Miner. **40**, 103–113 (1992). https://doi.org/10.1346/CCMN.1992.0400111
50. Schulze, D.G.: An introduction to soil mineralogy. In: Dixon, J.B., Schulze, D.G. (Eds.) Soil Mineralogy with Environmental Applications, pp. 1–35. Soil Science Society of America, Madison (2002). https://doi.org/10.2136/sssabookser7.c1
51. Schulze, D.G.: An introduction to soil mineralogy. In: Dixon, J.B., Weed, S.B. (Eds.) Minerals in Soil Environments, pp. 1–34. Soil Science Society of America, Madison (1989). https://doi.org/10.2136/sssabookser1.2ed.c1
52. Senthilvelan, T., Kanagaraj, J., Panda, R.C., Mandal, A.B.: Biodegradation of phenol by mixed microbial culture: an eco-friendly approach for the pollution reduction. Clean Technol. Environ. Policy **16**, 113–126 (2013)
53. Shen, S., Stucki, J.W., Boast, C.W.: Effects of structural iron reduction on the hydraulic conductivity of na-smectite. Clays Clay Miner. **40**, 381–386 (1992). https://doi.org/10.1346/CCMN.1992.0400402
54. Shi, C., et al.: Probing the interaction mechanism between oil droplets with asphaltenes and solid surfaces using AFM. J. Colloid Interface Sci. **558**, 173–181 (2019). https://doi.org/10.1016/j.jcis.2019.09.092
55. Singer, A.: Palygorskite and Sepiolite. Soil Science Society of America, 677 South Segoe Road, Madison, WI 53711, USA. Soil Mineralogy with Environmental Applications. SSSA Book Series, **7**, 555–583 (2002)
56. Sun, W. et al.: Molecular dynamics simulation of model asphaltenes between surfaces of varying polarity. Fuel **331**, 125842 (2023). https://doi.org/10.1016/j.fuel.2022.125842
57. Sun, W., et al.: Enhanced adsorption of anionic polymer on montmorillonite by divalent cations and the effect of salinity. J. Phys. Chem. A **125**, 1025–1035 (2021). https://doi.org/10.1021/acs.jpca.0c08797
58. Thompson, M.L., Ukrainczyk, L.: Micas. Soil science society of America, 677 South Segoe Road, Madison, WI 53711, USA. Soil Mineralogy with Environmental Applications. Vol. 7, pp. 431–466. SSSA Book Series
59. Van Bladel, R., Halen, H., Cloos, P.: Calcium–zinc and calcium–cadmium exchange in suspensions of various types of clays. Clay Miner. **28**, 33–38 (1993)
60. Wang, G., et al.: Utilization of methylene blue-adsorbed halloysite after carbonization to activate peroxymonosulfate degrading phenol: Performance and mechanism. Chemosphere **305**(2022), 135326 (2022). https://doi.org/10.1016/j.chemosphere.2022.135326
61. Wentworth, C.K.: A scale of grade and class terms for clastic sediments. J. Geol. **30**(5), 377–392 (1922). https://doi.org/10.1086/622910
62. White, G.N., Dixon, J.D.: Kaolin-Serpentine Minerals. Soil Science Society of America, 677 South Segoe Road, Madison, WI 53711, USA. Soil Mineralogy with Environmental Applications. SSSA Book Series, **7**, 389–414 (2002)
63. Ye, X., et al.: Effects of clay minerals on the transport of polystyrene nanoplastic in groundwater. Water Res. **223** 118978 (2022). https://doi.org/10.1016/j.watres.2022.118978
64. Zanardo, A., Marques Júnior, J.: Conceitos básicos em mineralogia. In: Química e Mineralogia do Solo, Parte I (Eds. Vander de Freitas Melo & Luís Reynaldo Ferracciú Alleoni). 695p. pp. 73–150 (2009)
65. Zelazny, L.W., et al.: Pyrophyllite-Talc Minerals. Soil Science Society of America, 677 South Segoe Road, Madison, WI 53711, USA. Soil Mineralogy with Environmental Applications. SSSA Book Series, **7**, 415–430 (2002)
66. Zhong, W., Wang, D., Wang, Z.: Distribution and potential ecological risk of 50 phenolic compounds in three rivers in Tianjin, China. Environ. Pollut. **235**, 121–128 (2018)

Computational Chemistry Tools for Atomic Level Investigation of Clay Composites

Francesco Ferrante

Abstract The most common computational methods used for the investigation of molecular and periodic systems will be briefly described, with particular emphasis on those approaches that could be employed for the study of clay structures at the atomistic level. The first part of the chapter is mainly dedicated to the conceptual basis of density functional theory and its implementation for molecular and periodic systems. The tight binding approximation to density functional theory and its modern variants, particularly suitable for atomistic studies of large systems, is treated as well. Classical molecular mechanics and molecular dynamics methods, as well as the definition of force fields suitable for clay materials, are shortly discussed. In the second part, case studies of application of computational approaches for the characterization of structures and properties of clay materials (in particular, the halloysite nanotube) are reported.

Keywords Density functional theory · Exchange–correlation functionals · Geometry optimization · Density functional tight binding · Molecular dynamics · Force fields · Halloysite nanotubes

1 Introduction

The extraordinary evolution of computational methods [1, 2], in particular those based on Density Functional Theory (DFT), combined with the power and technology of modern computers, as well as with the implementation of efficient algorithms into optimized codes, allows today the atomistic level investigation of systems having dimensions that were unimaginable even twenty years ago [3, 4]. Despite all this, those who want to study complex systems with a certain degree of confidence still must face many challenges, the first of them being to gain the experience needed to discriminate reliable computational results from useless numbers. Clearly this

---

F. Ferrante (✉)
Dipartimento di Fisica e Chimica “Emilio Segrè”, Università degli Studi di Palermo, Viale Delle Scienze Ed. 17, 90128 Palermo, Italy
e-mail: francesco.ferrante@unipa.it

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_3

experience cannot be acquired by merely reading this chapter, but I hope it will still be a pleasant reading that can stimulate the interested scientists to deepen the many aspects and formalisms that will be just mentioned, so that, if he/she wants, he/she can use them in the context of his/her own research or to better understand the research of others in this constantly evolving field. In what follows, after a brief introduction to the definition and calculation of molecular properties, to wave function-based computational methods and to the concepts behind density functional theory, some emphasis will be given to the computational approaches that can be used for the investigation of large systems, which could be of particular interest for the material scientists.

2 The Energy and the Born–Oppenheimer Surface

In the Born–Oppenheimer approximation, the total energy of a molecular system formed by N electrons and M nuclei is given by the energy of its electronic state plus the Coulomb repulsion energy between its nuclei

$$\mathrm{E}(\{R\}) = \mathrm{E}_{\mathrm{el}}(\mathrm{N}, \{R, \mathrm{Z}\}) + \sum_{\mathrm{A}=1}^{\mathrm{M}} \sum_{\mathrm{B}>\mathrm{A}}^{\mathrm{M}} \frac{\mathrm{Z}_{\mathrm{A}}\mathrm{Z}_{\mathrm{B}}}{|R_{\mathrm{A}} - R_{\mathrm{B}}|}, \tag{1}$$

where Z_{I} is the atomic number of nucleus I and atomic units are used. The value of the molecular energy depends on the position in space of all its nuclei, $\{\mathbf{R}\}$, i.e., what we commonly call the molecular geometry; Eq. (1) defines thus a hypersurface, known as Born–Oppenheimer (BO) potential energy surface, which forms not only the basis for the calculation of (not too exotic) molecular properties, but also the scenario from where extremely important chemical concepts originate, including just the concept of molecular geometry.

Years of research have shaped the abstract chemical intuition: Chemists can get an idea of the geometry even for the weirdest compounds. Unfortunately, an idea is not enough in order to calculate the vast majority of chemical and chemico-physical properties of molecular species; for this the researcher needs the exact values of distances, plane, and dihedral angles between the atomic nuclei in the molecule, where the "exact" term was used with the meaning "accurate enough, such that a larger accuracy does not affect the conclusion". As a matter of fact, the first thing to do before tackling any calculation is to find the possible molecular geometries. In practice, by starting from some educated guess of the geometry, which corresponds to a point in the BO surface, one can find the stationary point in the surface which is closer to that guess. If this point is a local or global minimum, a molecular conformation was achieved; a stationary point of the first order (a maximum along one direction, a minimum along all the others) is interpreted as a transition state (TS), while still no conventional meaning has been given to higher order stationary points. The search for minima and TSs is conceptually simple: they are points of the surface where no resulting forces act on the nuclei, so one can merely find those points where the nuclear gradients of the energy (1) are below a certain threshold close to zero. The algorithm, called geometry optimization, proceeds according to the flowchart reported in Fig. 1: the energy is calculated in the point $\{\mathbf{R}\}$ corresponding to the geometry starting guess, followed by the calculation of the nuclear gradient on the same point; if the gradient along all directions of minimization is smaller than a predefined value, the geometry is optimized; otherwise, the geometry is relaxed following the information on the forces acting on the nuclei obtained from the gradients and a new iteration starts. Once an optimized molecular geometry has been achieved, one must be sure that the nature of the stationary point is the one searched for. This information is readily given by the nuclear Hessian, i.e., the matrix of the second derivatives of the energy with respect to the nuclear coordinates: if the Hessian is definite positive, the geometry is a minimum on the BO surface; if the Hessian has only one negative eigenvalue, the stationary point is a transition state. Once calculated the Hessian, the harmonic vibrational normal modes' frequencies are available, which have a three-fold role: (i) must be used to add the zero-point vibrational energy (E_{ZPV}) to the molecular energy (1); (ii) can be used to simulate the IR spectrum of the investigated molecule (IR intensities are easily obtained); and (iii) can be used to calculate the vibrational partition function (Q_V), which together with the translational and rotational ones (Q_T, Q_R) allows to evaluate the absolute values of the thermodynamic quantities of formation, referred to the ideal state where all the nuclei and all the electrons forming the molecule are at infinite distance ones from the others. The value of E_{ZPV} in the case of TSs is used to estimate the activation energy barrier of the elementary steps of chemical reactions, that could be transformed to rate constants by means of the Eyring model (but beware of large error propagation). Those listed here and reported in Fig. 1 are only routinary molecular properties available from calculations; many others can be obtained as derivative of the molecular energy with respect to a perturbing physical entity.

Needless to say that, in order to use Eq. (1) for the calculation of molecular properties, one must have some way to evaluate the energy of, at least, the ground electronic state of the system: this is just the problem that quantum chemistry aims to solve.

3 A (Very) Brief Survey of Wave Function-Based Methods

The elementary unit of modern computational methods based on the wave function is the Slater determinant (SD); it is the determinant of a matrix whose elements are monoelectronic functions called spinorbitals, each spinorbital being the product of a molecular orbital and a spin function. For an N-electron system, a SD is formed by N occupied spinorbitals, with the electron label representing the row indexes and the spinorbital label representing the column indexes of a matrix.

In the Full Configuration Interaction (FCI) method, the wave function is written as a linear combination of all the unique, same-spin, same-symmetry NxN SDs which

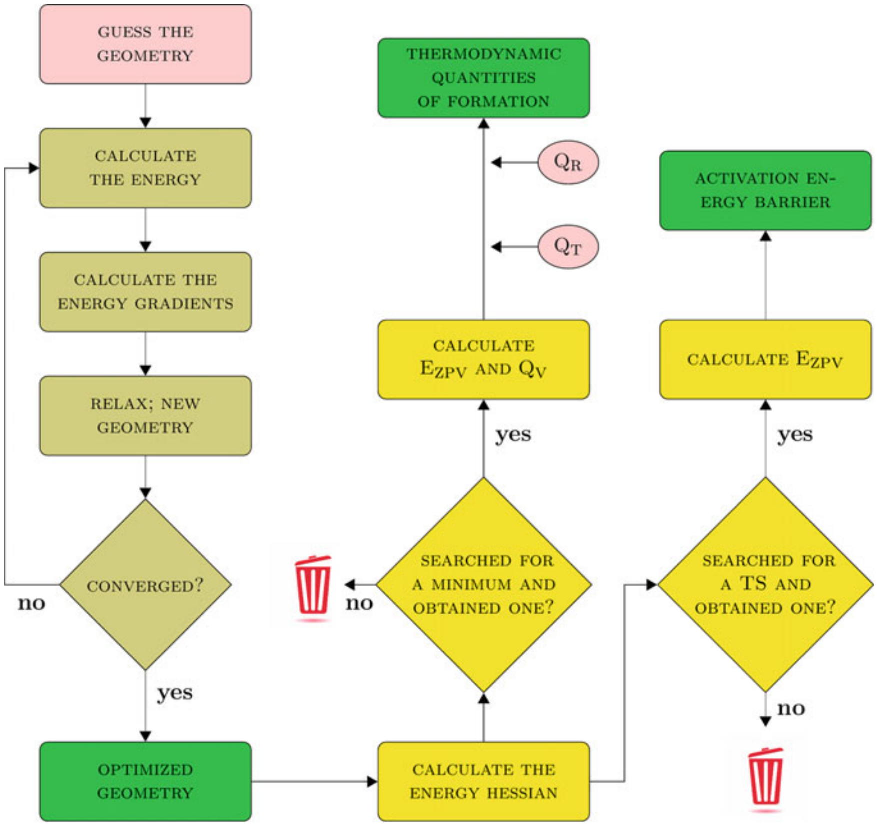


Fig. 1 Flowchart representing the cycle of the geometry optimization algorithm and the subsequent calculation of routine molecular properties

can be obtained by distributing N electrons in K spinorbitals. If K tends to infinity, the FCI wave function tends to the exact solution of the Schroedinger equation, and the associated energies would represent the exact non-relativistic energy values of the electronic states for the investigated system. Due to the extremely unfavorable scaling of the FCI computational cost with respect to N and K, up to date this method can be applied to nothing but the smallest molecules (diatomics of the first period elements) and it is commonly used as benchmark for approximated approaches. There are essentially two ways to obtain approximations to the FCI wave function. In the first series of methods, the number of electrons and of spin orbitals to which the FCI is applied is reduced by the appropriate definition of an active space (CAS-based methods); in the second, which includes historical methods like CISD, the number of determinant is reduced instead by truncation of the FCI expansion. One of the approaches with the largest accuracy/cost ratio, the CCSD(T) method, is within this second series; it is based on the so-called coupled cluster ansatz and is dubbed as the golden rule of computational chemistry. In this second series, we can find also the most drastic approximation, the Hartree–Fock (HF) method, according to which the wave function is expressed as a single SD. The method due to Douglas Hartree and Vladimir Fock is essentially the "father" of all ab initio approaches, and even if it is described here as an approximation to FCI, it is actually the method which gives the reference SD upon which all other approximations to FCI are constructed. Due to its monodeterminantal nature, which essentially means that the wave function is a antisymmetrized product of monoelectronic functions, the HF method suffers of the mean field approximation, where electrons' motion is not correlated (the probability of finding an electron in a certain point of the space does not depend on the probabilities associated to the other electrons); the difference between the exact non-relativistic energy and the HF one, always negative, is called correlation energy. HF method can be applied to very large systems (hundreds of atoms) but, because of the lacking of electron correlation, the HF results have an accuracy that is out of the modern standards. So a problem, common in computational science, appears: accurate method can be applied only to small systems, while large systems can only be treated with low accuracy. Density functional theory (DFT) solves this problem to some extent, allowing to obtain satisfactory results even on moderately large systems.

4 Density Functional Theory

Following the DFT formalism, the system energy is obtained as a sum of contributions determined from the integral over all spaces of some function of the ground-state electron density, $\rho(\mathbf{r})$, which, according to the first Hohenberg–Kohn theorem, contains all the information about the electronic states of the system at hand. The energy is exactly and rigorously defined as the sum of a contribution due to the interaction of the N-electron system with the nuclear charges, $V[\rho(\mathbf{r})]$, plus another contribution called Hohenberg–Kohn functional, $F^{HK}[\rho(\mathbf{r})]$. The form of F^{HK} is unknown and the strategy for DFT implementation is to extract from it all contributions that can be expressed as an integral involving $\rho(\mathbf{r})$, i.e., the Coulomb repulsion energy between two electron charge densities, $J[\rho(\mathbf{r})]$, and the kinetic energy of an idealized reference system of N non-interacting electrons which has, in every point of the space, the very same electron density of the real system, $T_S[\rho(\mathbf{r})]$. All other unknown contributions, namely the Coulomb and exchange–correlation energies and the correlation part of the kinetic energy, are collected in a new functional of the density, called the exchange–correlation functional, $E^{XC}[\rho(\mathbf{r})]$. The final expression for DFT energy is

$$\begin{aligned} E^{DFT}[\rho(r)] &= V[\rho(r)] + T_S[\rho(r)] + J[\rho(r)] + E^{XC}[\rho(r)] \\ &= -\sum_{A=1}^{M} Z_A \int \frac{\rho(r)}{|r-R_A|} dr + T_S[\rho(r)] + \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|r_1-r_2|} dr_1 dr_2 + E^{XC}[\rho(r)] \end{aligned} \quad (2)$$

In the implementation of DFT due to Walter Kohn and Lu Jeu Sham, the electron density of a N-electron system is written as a sum of one-electron charge probabilities

$$\rho(r) = \sum_{i=1}^{\mathrm{N}} \left|\theta_i^{\mathrm{KS}}(r)\right|^2, \tag{3}$$

where the $\theta^{\mathrm{KS}}(\mathbf{r})$ functions, called Kohn–Sham orbitals, are the DFT counterpart of the molecular orbitals of the Hartree–Fock theory. With this choice

$$\mathrm{T_S}[\rho(r)] = -\frac{1}{2}\sum_{i=1}^{\mathrm{N}} \int \theta_i(r)\nabla^2\theta_i(r)\mathrm{d}r. \tag{4}$$

In order to find the best Kohn–Sham orbitals, the variational theorem is used, according to which the best $\theta^{\mathrm{KS}}(\mathbf{r})$ functions are those giving an electron density to which corresponds the minimum energy for the investigated system in its electronic ground state. Then, the problem is solved by applying a minimization of the energy (2) with respect to the θ^{KS} functions, with the constraints that these functions remain always orthogonal to each other. This constrained functional minimization procedure leads to the following pseudo-eigenvalue Kohn–Sham equations

$$[-\frac{1}{2}\nabla^2 - \sum_{\mathrm{A}=1}^{\mathrm{M}} \frac{\mathrm{Z_A}}{|r - R_{\mathrm{A}}|} + \int \frac{\rho(r_2)}{|r - r_2|}\mathrm{d}r_2 + \frac{\delta \mathrm{E}^{\mathrm{XC}}}{\delta\rho(r)}]\theta_i^{\mathrm{KS}}(r) = \varepsilon_{ki}\theta_i^{\mathrm{KS}}(r) \tag{5}$$

which, since the operator within square brackets (called Kohn–Sham operator, f^{KS}) depends on the electron density, must be solved iteratively. Therefore, a form for the Kohn–Sham orbitals is guessed and the electron density is calculated from Eq. (3); knowing $\rho(\mathbf{r})$, f^{KS} is defined and Kohn–Sham equations can be solved to give updated forms for θ^{KS}. The iterations proceed until the variations in all the Kohn–Sham orbitals from a cycle to the next are under a given threshold. In practice, this procedure involving the solution of a integro-differential equation is substituted by an algebraic one simply by expanding the Kohn–Sham orbitals in terms of linear combinations of known functions, those collectively forming the basis set,

$$\theta_i^{\mathrm{KS}}(r) = \sum_{\mu=1}^{\mathrm{K}} \mathrm{c}_{\mu i}\varphi_\mu(r). \tag{6}$$

The basis set $\{\varphi\}$ is the second, fundamental ingredient which characterizes a quantum chemistry calculation. It is outside the scope of the present chapter to discuss deeply of basis sets, nor in treating the concepts defining their quality neither to give hints about the system characteristics one must take into account for a proper choice between one set or another. It suffices to say that, in the vast majority of molecular calculations, the basis set is formed by a certain number of contracted Gaussian-type orbitals (CGTOs), consisting of linear combinations of normalized atom-centered real solid harmonic Gaussian-type functions (called primitive), whose angular part defines the "angular momentum" of the CGTO and is taken from the corresponding atomic one-electron wave function

$$\varphi(r;\, R_{\mathrm{A}}, \mathrm{l}, \mathrm{m}) = \sum_{i=1}^{\mathrm{L}_c} \mathrm{d}_{\mu i}\, \mathrm{g}_i(r;\, R_{\mathrm{A}}, \mathrm{l}, \mathrm{m})$$

$$\mathrm{g}_i(r;\, R_{\mathrm{A}}, \mathrm{l}, \mathrm{m}) = \mathrm{N}_i |r - R_{\mathrm{A}}|^l \mathrm{e}^{-\alpha_i |r - R_{\mathrm{A}}|^2} \widetilde{\mathrm{Y}}_{\mathrm{l,m}}. \tag{7}$$

Here, $\mathrm{N_i}$ is the normalization factor, $\mathbf{R}_{\mathrm{A}}$ is the position vector of the nucleus A, and $\tilde{\mathrm{Y}}$ is the real or imaginary part (depending on m) of a spherical harmonic. The contraction coefficients $\mathrm{d}_{\mu\mathrm{i}}$ and the best "contraction scheme" (i.e., the number $\mathrm{L_c}$ of primitives for each function in the basis set) are commonly determined by means of dedicated atomic calculations, from where also the optimal Gaussian exponents, α_{i}, defining the radial part of each primitive, are obtained. Basis set is catalogued depending on the number and the role of the functions they contain. In strict variational methods, a larger number of functions in the basis set assures a more accurate value of the molecular energy (an infinite number is needed to reach the "limit" of a given method), but this assertion is not rigorously true in DFT. Large basis sets are essentially employed only for highly accurate post-Hartree–Fock calculations, while in common usage DFT approaches are joined to the so-called double-zeta plus polarization (DZP) basis sets. Even if smaller basis sets exist, DZP ones represent the minimum level accepted in today standards; if we use the concept of atomic orbital as can be found in standard chemistry textbooks, the DZP basis set is formed by one function for every core orbital and two functions for every valence orbital, plus one or more sets of additional functions having high angular moment, which are needed for the correct description of the electron cloud deformation (polarization) when an atom is within a molecular context. The most common DZP basis sets are those included in the families developed by Pople, Dunning, Ahlrichs, but many basis sets were proposed also for specific purposes, like the calculation of electric or magnetic properties, NMR shielding tensors, and so on. In material science, it is common to deal with heavy elements, like those from the fourth period onward: In this case, based on the rationale that chemistry properties are mostly determined by valence electrons, the common choice is to substitute the inner electron density with an effective core potential (ECP) and to use an explicit basis set only for the outermost electrons; the ECP will screen the nuclear charge and their effect is included in the nuclear attraction one-electron integrals (see expressions (11) below).

Returning to DFT, the linear combination coefficients $\mathrm{c}_{\mu i}$ of the expansion (6) now become the variational parameters and the Kohn–Sham Eq. (5) reduce to the corresponding matrix equation form

$$\mathrm{F}^{KS}\mathrm{C} = SC\varepsilon. \tag{8}$$

where $\mathbf{F}^{\mathrm{KS}}$ is the representative matrix of the Kohn–Sham operator in the $\{\varphi\}$ basis

$$\mathrm{F}_{\mu\nu}^{\mathrm{KS}} = \int \varphi_\mu(r)\mathrm{f}^{\mathrm{KS}}\varphi_\nu(r)\mathrm{d}r. \tag{9}$$

S is the overlap matrix

$$\mathrm{S}_{\mu\nu} = \int \varphi_\mu(r)\varphi_\nu(r)\mathrm{d}r. \tag{10}$$

C is the matrix whose i-th column contains the linear combination coefficients and ε is the diagonal matrix of the Lagrange multipliers $\varepsilon^{\mathrm{KS}}$. Equation (8) can be solved just like an eigenvalue equation (but iteratively) by using well-defined and very efficient algorithms, involving the calculation of one-electron integrals

$$-\frac{1}{2}\int \varphi_\mu(r)\nabla^2\varphi_\nu(r)\mathrm{d}r, \qquad \int \varphi_\mu(r)\frac{\mathrm{Z_A}}{|r-R_\mathrm{A}|}\varphi_\nu(r)\mathrm{d}r, \qquad \int \varphi_\mu(r)\frac{\delta \mathrm{E}^{\mathrm{XC}}}{\delta\rho(r)}\varphi_\nu(r)\mathrm{d}r \tag{11}$$

i.e., the kinetic energy, nuclear attraction, and exchange–correlation integrals, respectively, and the more expensive Coulomb repulsion two-electron integrals

$$\int \varphi_\mu(r_1)\varphi_\nu(r_1)\frac{1}{|r_1-r_2|}\varphi_\lambda(r_2)\varphi_\sigma(r_2)\mathrm{d}r_1\mathrm{d}r_2. \tag{12}$$

Who already knows the Hartree–Fock theory, or who is willing to study it from standard textbooks, will recognize that, even if they are based on different concepts, there is a strict analogy between the Kohn–Sham implementation of DFT and the Hartree–Fock formalism, and this is why the old computer programs able to calculate the HF energy were readily extended to DFT. As a matter of fact, the Kohn–Sham equations are very similar to the HF ones, with an important difference: the exact exchange energy contribution appearing in the Fock operator is replaced, in the Kohn–Sham operator, by the functional derivative of the exchange–correlation functional, introducing de facto Coulomb electron correlation, hence higher accuracy, in DFT. The equivalent of the matrix Eq. (8), in HF, is the famous Roothaan equations (of outmost importance for the historical development of computational chemistry), while, as a consequence of what said above, the third kind of one-electron integrals in (11) is replaced in HF by the exchange integrals, i.e., two-electron integrals that must be obtained from the Coulomb repulsion integrals by means of specific permutations. Just about the exchange–correlation integrals in DFT, it must be said that it has to be evaluated by means of some numerical quadrature technique, based on atom-centered grids of points and employing the numerical values of the basis set functions in these points.

At this point, it should be clear that the DFT problem can be solved only after having found a suitable description of E^{XC}, an issue that is at the heart of density functional theory; but how can one achieve a suitable description of something unknown? Apart from the knowledge of some characteristics that the exact exchange–correlation functional must have, its form is commonly chosen and adapted to reproduce well-defined experimental or highly accurately calculated data for various properties. This introduces some empiricism in DFT, that can be applied ab initio only after having defined possible parameters inside E^{XC}, but did not prevent this approach to become the most widely used in computational chemistry, being it applicable with confidence to large size systems (more or less those treatable with the Hartree–Fock method). The forms for E^{XC}, firstly proposed in the early 60s, were collected in two families: those functions depending only on the electron density (local density approximation, LDA) and those including also a dependence on the gradient of the electron density (generalized gradient approximation, GGA). However, the routinary use of DFT within the framework of molecular structure calculations can be traced back to 1993, when Becke found the way to introduce a portion of the exact Hartree–Fock exchange within the formalism, devising the so-called hybrid exchange–correlation functionals. Since then, researchers in the field proposed a lot of new functionals, most of them dedicated to alleviate some problems within DFT. As a matter of fact, DFT is plagued by two major problems: It does not reduce the accuracy problem on the description of dispersion interaction, already present in the HF method and whose solution would require the use of expensive highly correlated methods, and it fails to describe charge transfer electronic excitations. While some attempt was proposed to mitigate the second problem (e.g., range-separated functionals), new generation exchange–correlation functionals (meta-GGA, with empirical corrections, etc.) seem to be fruitful on solving the first one, that can be important in computational material science. In particular, the very cheap and efficient correction due to Grimme is becoming an essential ingredient of all functionals.

The trend today is to relegate the use of post-Hartree–Fock method to very small systems, in particular when one wants to investigate properties requiring high (chemical or more) accuracy, such as spectroscopic constants, atomization energies; coupled cluster is the method of choice if the static correlation (that due to the fact that two or more electron configurations are equivalent or nearly-equivalent) in the investigated molecule can be regarded as negligible; otherwise, some CAS-based approach, followed by a multireference method, must be applied. For medium–large molecules, reaction kinetics, periodic calculations, ab initio molecular dynamics simulations and such, density functional theory, preferably with a dispersion-corrected exchange–correlation functional, are the only formalism to employ, at least until some new coupled cluster variant becomes usable for large molecules.

5 Density Functional Tight Binding

But what if the system size is so large that even DFT becomes not affordable? This is indeed common in material science and it is clear that in these cases some compromise must be accepted in terms of the desired accuracy. This said, one can wonder which computational approach could be used for very large systems. In the first years of quantum chemistry, when calculations were prohibitive also for medium size molecules, a plethora of empirical and semiempirical methods arose. Starting from the simple Huckel method, from where chemists presumably developed their, sometimes too naive, vision of molecular electronic structure, in these kind of approaches, together with the introduction of crude approximations within the Hartree–Fock theory, there is the substitution of the expensive computation of most electronic integrals, in particular the two-electron ones, with some kind of atomic parameters. The implementation of these methods, therefore, required tables containing the atomic and atomic-type parameters, obtained in a number of ways but always outside from the method itself (which was therefore never ab initio). The ideas behind semiempirical methods developed enormously and those approaches which still survive (most of them are used no more) reached a remarkable degree of sophistication, which allows some confidence for their application to large size systems. However, just as Hartree–Fock method was superseded by density functional theory, so semiempirical methods based on approximate HF treatments have left the place to approximate DFT descriptions, one and for all the so-called density functional tight binding (DFTB) approach. In the DFTB formalism [5], a reference electron density is defined as a superposition of the electron densities of the isolated neutral atoms forming the investigated molecule and the molecular energy is expanded at a given order in the electron density fluctuation, $\delta\rho(\mathbf{r})$. As happened for DFT, also the DFTB method was for a long time mainly confined within applications to solid state, until a newly proposed variant made it successfully applicable for molecular systems. This variant is the self-consistent-charge density functional tight binding (SCC-DFTB) approach, according to which the system energy is expressed as the following expansion to second order in $\delta\rho(\mathbf{r})$

$$\begin{aligned} \mathrm{E}^{\mathrm{DFTB}} &= \sum_i \mathrm{n}_i \int \theta_i(r)\mathrm{H}_0^{\mathrm{KS}}\theta_i(r)\mathrm{d}r + \mathrm{E}^{\mathrm{REP}} \\ &+\tfrac{1}{2}\int \tfrac{\delta\rho(r)\delta\rho(r')}{|r-r'|}\mathrm{d}r\mathrm{d}r' + \tfrac{1}{2}\int \delta\rho(r)\tfrac{\delta^2\mathrm{E}^{\mathrm{XC}}}{\delta\rho(r)\delta\rho(r')}\delta\rho(r')\mathrm{d}r\mathrm{d}r' \end{aligned} \tag{13}$$

where $\mathrm{n_i}$ is the occupation number of the i-th θ orbital and $\mathrm{H_0}^{\mathrm{KS}}$ is the tight binding Hamiltonian. A number of approximations leads to the parameterized expression

$$\mathrm{E}^{\mathrm{DFTB}} = \sum_{i\mu\nu} \mathrm{n}_i \mathrm{c}_{\mu i}\mathrm{c}_{\nu i}\mathrm{H}^0_{\mu\nu} + \sum_{ab}\mathrm{U}_{ab} + \frac{1}{2}\sum_{ab}\gamma_{ab}\Delta\mathrm{q}_a\Delta\mathrm{q}_B, \tag{14}$$

where the first term is obtained from the corresponding term in (13), after the θ functions have been substituted by a linear combination of atomic orbitals (obtained by solving the so-called pseudo-atom equation, containing a confinement parameter). The sum of U_{ab} terms approximates the repulsive E^{REP} energy contribution; the U_{ab} pair potentials, depending on the distance between the centers a and b, are parameters specific to every possible couple of atoms in the investigated molecule and are obtained by a fitting procedure based on the difference between E^{DFTB} and DFT reference energies calculated as a function of the distance of atoms a and b in simple interacting molecules. Finally, the last term in (14) collects the last two terms in (13) and describes them as fluctuations of the atomic Mulliken charges q as a function of molecular geometry, with the γ_{aa} parameters correlated to the difference between the ionization potential and the electron affinity of atom a, and the γ_{ab} parameters expressed in analytic form by a damped Coulomb potential.

In further developments, the energy is expanded to third order, which seems to give better results for dispersion interactions. Apart this, however, the DFTB approach is plagued by the need of too specific parameters, whose transferability is hardly guaranteed. One could get around this obstacle by generating parameters appropriate only for specific systems and purposes, which is what is generally done, but this generation is too involved and arbitrary to some extent. It is true that the Extended Tight Binding (XTB) formalism and all its variants, recently proposed by Grimme, are free from atomic-pair-specific parameters and therefore are the optimal candidates to achieve the leading position between the semiempirical approaches, but this method still need some testing for general applicability.

6 Hybrid Methods

If a molecular system is formed by hundreds or thousands of atoms, it is in some cases possible that the property we are interested in is localized in a determined portion of the molecule, while the influence of the remaining part can be viewed as a substituent effect. Clearly, this is not the case if one wants to investigate the secondary structure of a small protein, but some useful informations can be acquired on the local interactions determining that secondary structure. The approach to use in such cases was pioneered by Morokuma in1995, when, by collecting and improving earlier ideas, he proposed the ONIOM method. According to this approach, the system to investigate is divided in two or more well-defined regions which are related one to the other by an inclusion relationship. One of these regions (the “model system” M) is the molecular portion considered the most responsible of a given property of interest; in the two-layer version of ONIOM, M is included in the entire molecule (indicated as “real system”, R), while in the three-layer version, M is included in an intermediate system, I, which is in turn embedded in R. Now, a high accuracy computational method H is chosen which can be applied to the model system, followed by a medium accuracy method, m, that can be applied to the intermediate system, if any, and a low-level method, L, that can treat the entire real system. By indicating with E(A,

B) the energy of a system A treated with the computational method B, the energy E(R, H) which is the uncomputable energy of the whole molecule at high accuracy is extrapolated as E(M, H) + E(R, L) − E(R, L), for Oniom-2 layer, or as E(M, H) + E(I, m) + E(R, L) − E(M, m) − E(I, L) for the three-layer variant, i.e., E(R, H) is evaluated by means of affordable only calculations. The expression of the target energy as a sum of independent contributions, joined to a proper treatment of the link atoms, i.e., those atoms (generally hydrogen) introduced on the edge of model and intermediate systems in order to saturate the dangling bonds originated from the cut and make them suitable for a standalone calculation, makes possible the evaluation of ONIOM energy nuclear derivatives, essential for the analytical geometry optimization and vibrational frequency calculation, thus allowing a very fruitful employment of this approach.

A specific, somehow crafty usage of the ONIOM concept is the building of a necessary framework around a portion of a very large molecule or even of a periodic system. The issue is better explained with an example. Consider one wants to investigate the adsorption of a given molecule on the inner wall of a zeolite cage, let us say the wall of the larger channel in the beta zeolite. Taking into account the wall thickness, the region of this channel is defined by ca. 80 silicon tetrahedra, giving a total of ca. 250 atomic centers. Such a supercell hardly can be the subject of accurate calculations, but the problem becomes prohibitive if one wants to avoid spurious interactions of the adsorbed molecule with its periodic images, so that the supercell must be doubled. A way to treat the problem could be to define a minimal inner surface, i.e., the smallest surface that can accommodate the molecule whose adsorption characteristic are desired, and cut it from the zeolite structure, having care to saturate with hydrogen the dangling bonds originated from the cutting. The system so created should be subjected at least to geometry optimization, to discover the adsorption geometry. Doing so, however, the adsorbing surface would relax, and it will be no more representative of the zeolite largest channel wall. Indeed, that portion of the surface has the correct geometry only if it is embedded in the zeolite framework. Being the use of a larger supercell prohibitive, it could be a natural choice to couple the DFT approach employed for the portion of interest to a semiempirical, or better a molecular mechanics force field, according to ONIOM prescription, the embedding assuring to some extent no spurious distortion of the channel surface. It is trivial to say that, just as in all other cases in which computational chemistry approaches are used, preliminary investigations must be afforded to test the reliability of the model and have some confidence with the results obtained.

7 The Approaches for Periodic Systems

Let us take a look now to the quantum chemical approaches that can be used to treat the solid state. According to Bloch theorem, a function which approximately describes the probability amplitude of finding an electron in a certain point of the space, when it is subjected to a the periodic potential generated by an infinite lattice of positive charges and to the mean field repulsion of all other electrons, can be expressed in the form

$$\xi_{\mu k}(r) = \mathrm{U}_{\mu k}(r)\mathrm{e}^{ik\cdot r}. \tag{15}$$

where the U functions have the same periodicity of the crystal lattice, represented by the vector $\mathbf{L} = \mathrm{n}_1\mathbf{a_1} + \mathrm{n}_2\mathbf{a_2} + \mathrm{n}_3\mathbf{a_3}$, being $\mathbf{a_1}$, $\mathbf{a_2}$,$\mathbf{a_3}$ the three lattice vectors, and $\mathbf{k}$ is a reciprocal space vector inside the so-called first Brillouin zone (BZ). In the DFT context, this means that the solutions of the Kohn–Sham Eq. (5) must satisfy the following constraint:

$$\xi_{\mu k}(r + L) = e^{ik\cdot r}\xi_{\mu k}(r). \tag{16}$$

The most natural choice for the expansion of the ξ functions is a linear combination of plane waves

$$\xi_{\mu k}(r) = \sum_G a_k(G)e^{i(k+G)\cdot r}. \tag{17}$$

where the summation is extended to all the reciprocal space vectors $\mathbf{G}$ selected from a grid and includes all the plane waves having kinetic energy below a certain cutoff. Since in order to reproduce the local form of the ξ functions prohibitively high values of the cutoff should be necessary, only the valence regions of the atoms are explicitly considered, inner regions being described by appropriate pseudopotentials. Finally, the electron density needed in the KS equations is defined and calculated on a grid of points belonging to the first Brillouin zone, according to the sampling proposed by Monkhorst and Pack:

$$\rho(r) = \frac{1}{V_{BZ}}\sum_{\mu=1}^{n}\int_{\mathrm{BZ}}\xi^*_{\mu k}(r)\xi_{\mu k}(r)\mathrm{d}k \simeq \frac{1}{V_{BZ}}\sum_{\mu=1}^{n}\sum_{k\in\mathrm{BZ}}\xi^*_{\mu k}(r)\xi_{\mu k}(r). \tag{18}$$

The expansion in terms of plane waves according to Eq. (17) is certainly the most used and is implemented in the most common software's for periodic DFT calculations, such as VASP and AbInit, but is not the only possible choice. In the Crystal program, Gaussian basis sets are employed while the SIESTA code, which implements the homonym computational method and in the first years of 2000s represented a breakthrough in this field, efficiently uses appositely generated numerical atomic orbitals whose quality can be tuned. From a periodic calculation on a crystal lattice (whose symmetry characteristics commonly come from the experiment), useful informations can be obtained: electronic bands, energy gap and conducting properties, cell geometries, density of states (from which one can extract information such as the number of mobile states for electric conductivity), phonon dispersion relations, elastic properties, etc. However, there are very important chemical processes (one and for all, heterogeneous catalysis) which do not occur in the infinitely self-replicating bulk of the crystal, but on regions where lattice periodicity is broken: the crystal surfaces. What is the approach to use in order to investigate a portion which is located at the interface between a semi-infinite periodic crystal and the vacuum? In the most intuitive approach, the system is still periodic in three dimensions, but the cell vector normal to the surface object of investigation is artificially elongated to assure a vacuum (typically 30 Å); along the other two directions and the direction opposite to the vacuum, the unit cell is replicated, with unchanged lattice constants, a number of times sufficient to create a slab, which is treated as a supercell to replicate periodically. In this slab approach, care should be taken to have some issues always under control: (i) the slab should be large enough to avoid spurious, unwanted interactions between a molecule adsorbed or reacting on the surface and its periodic replicas; (ii) the slab should be thick enough to mimic the semi-infinite bulk below the surface and its polarizing effect; (iii) for semiconductors it is necessary to saturate the dangling bonds in the underneath surface; (iv) energy should be corrected to eliminate the fictitious dipole-dipole interaction originated by slab creation. Alternatively, the cluster, not periodic, approach can be employed. In this case, the vacuum above the surface is guaranteed and lateral interactions cannot occur; further, being outside from the field of periodic calculations, one can take advantage of the wider choice of methods proper of molecular calculations (e.g., hybrid exchange–correlation functionals and tailored basis sets), not to mention the availability of energy gradients which greatly facilitates the quest for transition states in chemical reactions (for transition states in periodic investigations numerical approaches must be used instead, such those based on the Nudged Elastic Band method). However, the cluster approach has its own problematic deficiencies, such the possible occurrence of strong border effects and the unnatural structural relaxation of the whole system. Obviously, the last sentence is true if one wants to describe a crystal surface by using a cluster as model, but those mentioned become physical characteristics of the system if the object of the investigation is a true, physical cluster of atoms.

8 Molecular Dynamics Simulations

Just some rows above, the word “force field” came into play. Even if it could be applied in a wider context, this term was used here to introduce the models of classical molecular mechanics (CMM) and molecular dynamics (CMD) and explore if there is some room for their use in material science. By using the term “classic”, it is intended that the treatment of the molecular systems occurs outside the realm of quantum mechanics; so, electrons are no more considered explicitly, but their presence is incorporated inside fictitious parameters, representing, e.g., the force of a given chemical bond. Energy is here calculated as a sum of parameterized contributions, commonly grouped in internal (bond stretch, bending, etc.) and external (Coulomb, van der Walls interactions, and so on) to the molecular entity. The union between (i) the nature of the contribution to the energy, (ii) the formula chosen for the calculations of each contribution, and (iii) the set of all the atom-type and contribution-type specific parameters forms a force field. As an example, one of the most diffuse force fields is the AMBER one, which defines the energy of a M-atoms molecule as

$$\begin{aligned}\mathrm{E} = &\sum_{\text{bonds}} \frac{1}{2}\mathrm{K}_b(r-\mathrm{r}_0)^2 + \sum_{\text{angles}} \frac{1}{2}\mathrm{K}_a(\theta-\theta_0)^2 + \sum_{\text{torsions}} \frac{1}{2}\mathrm{V}_t[1+\cos(n\omega-\gamma)] \\ &+ \sum_{i=1}^{M-1}\sum_{j=i+1}^{M} \frac{\mathrm{q}_i\mathrm{q}_j}{4\pi\epsilon_0|r_i-r_j|} + \sum_{i=1}^{M-1}\sum_{j=i+1}^{M} \varepsilon_{ij}[(\frac{\sigma_{ij}}{|r_i-r_j|})^{12} - 2(\frac{\sigma_{ij}}{|r_i-r_j|})^{6}].\end{aligned} \tag{19}$$

where the first term defines the contribution of bonds stretching, written as a harmonic potential depending on the interatomic distance r and containing two parameters: the harmonic force constant for the given bond, $\mathrm{K_b}$, and its equilibrium length, $\mathrm{r_0}$. Similarly, the second contribution is that due to bond angles bending, with obvious symbols, while the third collects the energetic terms related to variations in the torsional angles. Electrostatic interactions between atoms in the same or in different molecules are described by a simple Coulomb potential between fictitious atom-centered partial charges q, and dispersion interactions are entrusted to a 12-6 Lennard–Jones potential, with its famous pair parameters ε and σ. These last two contributions run over all possible couples of atomic centers in the investigated system. The atom-type and pair parameters are to be determined by some procedures which could involve well-defined experimental data, equation of states, dedicated experiments, ab initio calculations, and so on. Transferability is sometimes assured between parameters for molecules belonging to classes of homologue systems (e.g., proteins, DNA, sugars), but commonly a force field cannot be considered of general applicability, so that a very large number of new force fields (as well as extension/variation/recalibration of existing ones) suitable for particular purposes are continuously proposed to the scientific community. For example, based on the AMBER force field but without the torsional term, the CLAYFF is parameterized on purpose for the investigation of the clay–water interface.

Force field-based approaches can be used for geometry optimization by simply calculating the energy of a certain molecular geometry and relaxing it according to the force on every atom, and this is the way it is used for assuring the embedding of the molecular portion in ONIOM calculation. More often, on the other hand, the force fields are used for the time evolution of systems (particularly in the condensed phase), by discretizing the physical time in appropriate timesteps (in the order of femtoseconds) and exploiting the forces obtained from the force field in efficient algorithms (e.g., velocity Verlet) which propagate the system according to classical Newton or Lagrange equations. One speaks in these cases of classical molecular dynamics simulations. Dedicated calculation centers can afford CMD simulation for relatively long times (μs) or very large system size (billion of atoms), but it is clear that the results must be trusted in the view of ensemble properties, being useless here to search for accuracy on the details. The quantum-mechanics counterparts, like Born–Oppenheimer molecular dynamics or the Carr–Parrinello approach, where the forces between atomic centers can be calculated ab initio from the potential due to the electrons, are conversely full of details, but are applicable only to small systems for very short simulation times.

9 Case Studies: Halloysite Nanotubes

Halloysite nanotubes (HNTs) are natural clay materials first described in 1826 by Berthier. They have peculiar spiral morphologies conferred by the rolling up of kaolinite-like sheets, composed by a layer of SiO_4 tetrahedra (which will form the outer surface of the nanotube) joined to a layer of AlO_6 octahedra (representing the inner surface). The HNT stoichiometry, $Al_2Si_2O_5(OH)_4 \cdot nH_2O$, allows to distinguish a hydrated form (n = 2, indicated as HNT-10 Å), bearing interarms water molecules, and a dehydrated one (n = 0, HNT-7 Å). Relegated for a long time to a use almost exclusively relevant to the ceramics industry, in the last fifteen years HNTs started to become important as a cheap and eco-friendly material for a number of applications, ranging from controlled release to nanocarrier for active compounds, from design of polymeric nanocomposites to catalysis.

The computational characterization at atomistic level of HNT composite must face many challenges. Let us imagine one wants to investigate the hydrogen bonds network which realizes in the region comprised between the spiral arms of a halloysite-10 Å nanotube. Here, there are H-bond interactions between the water molecules and between them and the two surfaces of HNT. The spiral structure of HNTs gives rise to serious problems for the simulation and the first of them is merely the construction of the input system geometry. It may sound trivial, but every calculation approach needs a molecular geometry to begin with: many free or commercial software's are indeed devoted to the graphical construction of molecules to be used as input geometry, but when one treats large size systems, it is clear that some automatism must be devised. A vast number of codes are dedicated to the building, visualization, and analysis of unit cells of given symmetry for periodic calculations, or for the construction of polypeptides given the list of the amino acid residuals in the chain, or the generation of carbon nanotubes and alike given the chirality. HNTs, however, cannot be built using codes for periodic systems, since they are periodic only in the direction of the rolling axis. As a matter of fact, the spiral has a curvature which changes from point to point, so no exact periodicity of a unit cell can occur along its arms. One artifact could be to forget the spiral structure and use a multiwalled cylindrical model for HNT, but, as will be discussed below, this could cause the missing of some features related just to the spiral architecture. It is better to assume that HNT can be generated by starting from a reference regular lattice of points arranged on the arms of an Archimedean spiral, whose polar equation is $r(\theta)=a+b\theta$. The lattice points can be placed on the spiral by exploiting the formula for the spiral arc length

$$s(\theta) = \frac{1}{2}b\left[\theta\sqrt{1+\theta^2} + \ln\left(\theta + \sqrt{1+\theta^2}\right)\right]. \qquad (20)$$

An appropriate repetition unit is now convoluted with every lattice point (see Fig. 2), opportunely rotated and slightly adjusted according to a correction angle determined from the spiral curvature in that point (which decreases smoothly along the arms).

$$\kappa(\theta) = \frac{2+\theta^2}{b\left(1+\theta^2\right)^{3/2}}. \tag{21}$$

This approach works well unless the curvature is too pronounced, but this should be never the case since the HNT model must have a relatively large inner cavity; hence, the phase of the spiral is never too small. Clearly, the model constructed this way is only the starting point for geometry optimization. As a matter of fact, after having generated the HNT supercell, one must face the problems related to its dimension: even a small supercell corresponding to the section of a HNT-10 Å having a modest 5 nm inner cavity diameter, and formed by spiral arms that overlap

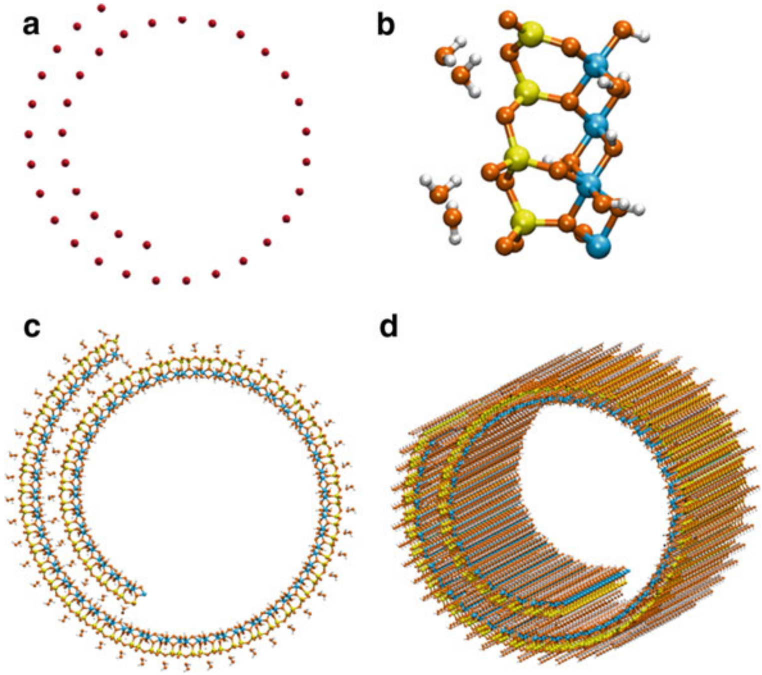


Fig. 2 **a** Archimedean spiral lattice of points defined by spiral parameters such that the inner diameter-like distance is close to 10 nm and the interarms' spacing is enough to give HNT-10 Å. **b** An appropriate repetition unit formed by a Si–O layer connected to a Al–O one and four water molecules, with stoichiometry $H_{15}Si_4Al_4O_{24}$; color code: yellow = Si, cyan = Al, orange = O, white = H. **c** The HNT-10 Å input supercell as the result of the convolution of the repetition unit with the spiral lattice, followed by a rotation whose entity depends on the lattice point. **d** The HNT-10 Å spiral nanotube obtained by periodic repetition of the supercell along the rolling axis

for one half, has ca. 1400 atoms if an armchair rolling is chosen, a number which increases to more than 2000 when the opposite limiting zig-zag rolling direction must be considered. Such a supercell can be periodically replicated along the nanotube axis by using the appropriate cell vector length, while vacuum must be assured in the other two perpendicular directions. This system is too large to be treated with ab initio methods, but its dimension is within the applicability range of semiempirical approaches like, e.g., SCC-DFTB. If this is the case, the *matsci* set of Slater–Koster parameters could be used, which was realized to treat systems containing common elements in material science. Concerning the code to use to perform the calculation, as a guideline I suggest to employ whenever possible software's dedicated to the implementation of only one kind of computational approach instead of general ones; so in this case, the choice could be the DFTB+ program developed by Aradi and coworkers.

Geometry optimization of the HNT-10 Å supercell reveals some features connected to the intrinsic disorder of the spiral architecture. In order to discuss these ones, let make a comparison with a hypothetical system formed by water molecules sandwiched between two planar kaolinite layers, i.e., let unroll the HNT-10 Å. In this case a perfect periodicity is present in the system: all tetrahedral silicon centers have equal geometry, the same holds true for the octahedral aluminum centers and, from a structural point of view, a regular network of hydrogen bonds would occur between the water molecules, and between them and the upper and lower surfaces. The transformation of this system to the spiral HNT-10 Å causes non-periodic distortions of the SiO_4 and AlO_6 geometries along the arms and calculation revealed that (at least for the idealized system investigated) the less amount of energy required seems to occur in spiral arrangements where relatively large distortions are localized in a limited number of points along the arms, joined to very small distortions in all other points. This sort of polygonal spiral would be preferred to a smoother one where distortions would be distributed between all the SiO_4 and AlO_6 centers. Further, the characteristics of the hydrogen bonds network in the unrolled HNT originated from the fact that the water layer was comprised between a periodic SiO surface and a periodic AlO ones. In the spiral HNT-10 Å, on the other hand, the water molecules experience the disordered environment in which they are enclosed; as a consequence, a large variety of hydrogen bond configurations can take place and the water molecules would adapt in order to provide the best interactions. Still, at a given temperature, the H-bonds' configurations can change over time, giving rise to a dynamic linkage between the arms of the halloysite nanotube, whose characteristics could be investigated in terms of pair correlation functions after that a dedicated molecular dynamics simulation is performed. The occurrence of the adaptive and dynamic H-bond network, originated from the natural disorder related to the spiral structure, could be one of the reasons why HNT-10 Å exists instead of a lamellar kaolinite with water between adjacent layers.

After having investigated the HNT model in its integrity, one could be interested to nanocomposites involving modified or functionalized HNTs for specific applications, and this constitutes another challenge, to tackle which one must resort to the usual compromises. To alleviate the burden, it can be considered that many applications of halloysite-based composites depend on the interactions or reactions of its outer and inner surfaces with molecules of interest. Then, most of the cases can be investigated by using local models of HNT instead of the whole nanotube. Conversely, it must be taken into consideration that now we must go into the details of interactions, adsorption geometries, local distortions, bonds breakings and formations, activation barriers, etc.; therefore, quantitative informations are needed if one wants to be predictive, and resorting to accurate DFT approaches cannot be avoided. Since this is expensive (or even impossible) both in terms of time and resources, a suitable choice must be done. A common way to proceed could be to tailor a portion of surface from the nanotube model. What could be a representative portion in terms of lateral extension and thickness would heavily depends on the nature of the system and on the properties the investigator is interested on but, again, the choice is sometimes restricted to what can be treated by DFT. One could assume that a coronene-like surface portion formed by 24 silicon tetrahedra and the same number of aluminum octahedra (depicted in Fig. 3) could represent a good, minimax, choice, for e.g., the adsorption of one molecule, or the surface modification with one molecular fragment. It could be treated as the model system of a ONIOM calculation or as a standalone molecule; in both cases, the DFT calculation would be performed using a HNT portion with $Al_{24}Si_{24}O_{126}H_{48}$ stoichiometry, where the additional hydrogen atoms would come from the need to saturate the dangling bonds originated by the cut (which is the role of the linking atoms in ONIOM). In order to obtain a reliable description of dispersion forces, one could use the B3LYP-D3 exchange–correlation functional, i.e., a hybrid one with Grimme correction; however, if one wants to take advantage of the resolution of identity approximation, a pure exchange–correlation functional should be used, in which case the choice could fall on some Minnesota functional, such as the M06-L. The basis set must be obviously of double-zeta quality plus polarization. If an ONIOM approach is employed, the high-level DFT method can be joined to a molecular mechanics force field (as CLAYFF, or the Universal Force Field, UFF) as low-level method. If instead the portion is investigated as a standalone unit, the user should pay attention to freeze the positions of some non-influent atomic centers (e.g., those on the borders); otherwise, the portion will distort and the spiral local curvature will be lost. Taking into account that a molecule of, say, 20–30 atoms is to be adsorbed on the HNT portion, the DFT geometry optimization of the entire system will take from 2 to 6 days on 32 shared-memory new generation processors.

10 Final Remarks

Computational chemistry is an extremely important resource of modern science, which can work in synergy with the experiment. It can be useful for developing basic knowledge, for the interpretation of data and trends, for the prediction of the characteristics of new molecules or of the behavior of already known molecules in new or unusual conditions. It can be applied in essentially all fields of chemistry. However, before starting his/her computational work, the researcher who intends to

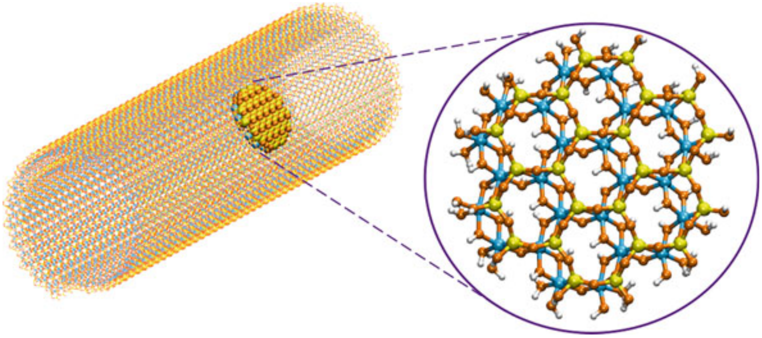


Fig. 3 Nanotube portion with $Al_{24}Si_{24}O_{126}H_{48}$ stoichiometry, which could be used as a model to investigate the possible modification of the outer and inner surfaces of halloysite. Color code: yellow = Si, cyan = Al, orange = O, white = H

practice calculations should ask himself/herself the following set of questions: why do I want to make calculations on this system? Have I well identified the problem I want to investigate? Can I obtain the answers I need? What accuracy do I need? The one required to reproduce, for example, the rotational spectrum of a molecule is far greater than that commonly used to describe a reaction mechanism. In addition to being necessary to establish a correct way to proceed, having these issues clear helps to understand which methods, among the many available, should be used. It must be borne in mind that some types of computational investigations may be impossible, at least today, and that sometimes one could be satisfied with evaluating trends: the exact value of a particular quantity that refers to a physical property could be only a detail.

References

1. Cramer, C.J.: Essentials of Computational Chemistry—Theories and Models, 2nd edn. Wiley
2. Young, D.: Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems. Wiley-interscience
3. Lee, J.G.: Computational Materials Science—An Introduction, 2nd edn. CRC Press
4. Ohno, K., Esfarjani, K., Kawazoe, Y.: Computational Materials Science—From Ab Initio to Monte Carlo Methods. Springer
5. Spiegelman, F., Tarrat, N., Cuny, J., Dontot, L., Posenitskiy, E., Marti, C., Sikmon, A., Rapacioli, M.: Density-functional tight-binding: basic concepts and applications to molecules and clusters. Adv. Phys. X **5**(1), 1710252 (2019)

Advances in the Development and Applications of Clay-Based Composites

Munir Ahmad, Umair Riaz, Shazia Iqbal, Hina Rasheed, Mohammed Awad Mousa Mousa, Abdullah S. F. Al-Farraj, and Mohammad I. Al-Wabel

Abstract Natural clay minerals are known for their unique characteristics such as higher surface area and cation exchange capacity, layered structure, and porosity. However, due to negative surface charges and crystal structure, the widespread applications of natural inorganic clays are limited. Therefore, fabrication of clay-based composite materials has gained significant attention of researchers in recent times owing to enhanced physiochemical properties and structural composition as compared to the pristine natural clay minerals. Clay-based composites can be fabricated through combining clay minerals with the foreign materials via intercalation, mixing and/or exfoliation to tune the characteristics of clay for target applications. Modification of natural clay minerals and generation of clay composites have found a variety of new and interesting applications in various sectors due to improved physiochemical and structural properties. Therefore, the new trends in the application of clay-based composites have been reviewed and discussed in this chapter. The utilization of clay composites in environment, energy, agriculture, biomedical, and industry sectors has been discussed in detail.

Keywords Clay composite · Adsorbent · Energy · Modification · Biomedical

---

M. Ahmad · M. A. Mousa Mousa · A. S. F. Al-Farraj · M. I. Al-Wabel (✉)
Soil Sciences Department, College of Food and Agricultural Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia
e-mail: malwabel@ksu.edu.sa

U. Riaz
Department of Soil and Environmental Sciences, MNS University of Agriculture, Multan, Pakistan

S. Iqbal
Department of Soil Science, University of Sargodha, Sargodha, Pakistan

H. Rasheed
Department of Soil Science, The Islamia University of Bahawalpur, Bahawalpur 63100, Pakistan

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_4

1 Introduction

The natural clay minerals often comprise hectorite, montmorillonite, laponite, zeolite, sepiolite, rectorite, saponite, vermiculite, kaolinite, and chlorite, which are generally occurred as hydrous aluminum phyllosilicates having iron, alkali metals, magnesium, and other cations [1]. Generally, the performance of clay minerals depends on the fundamental characteristics including surface area, porosity, pH, modifications, mineral types, as well as chemical and structural composition [2]. However, the occurrence of negative surface charges and the crystal structure of clays hinder their performance for environmental, industrial, and agricultural applications [2]. Moreover, the amount of exchangeable ions, texture quality, and soluble salts present in the clay minerals influence the performance and properties of the natural clay minerals. Isomorphic substitution and cations present in the sheets result in charge deficit, which varies with minerals creating different technical issues. Furthermore, the amount of non-clay minerals and heavy metals present in the clay minerals may affect their application and performance [3]. For instance, Xi et al. [4] reported that natural clay minerals are not suitable for the removal of anionic pollutants specifically inorganic oxyanions, i.e., chromate, nitrate, and arsenate from the contaminated media owing to the negative charges present on the surface of clay minerals, which repel such anions. Less reactivity, less adsorption capacity, and less surface area have also been observed in natural clay application [5]. It has been reported that the negative charge present on bentonite resulted in the charge repulsion and reduced the removal of diazo dye [6, 7]. Furthermore, the colloidal characteristics and micro-sized particles are other factors responsible for restraining the regeneration and reuse of natural clays in wastewater treatment [2]. Although, the natural clay minerals are being used as efficient adsorbents in present era due to their cost-effectiveness, easy handling, efficiency, and eco-friendliness; nonetheless, still there are some issues related to them which need to be addressed while considering them for the removal of pollutants from aqueous medium. Therefore, the aforementioned factors must be considered before using the clay minerals' environmental and industrial use.

Natural clay minerals contain a mixture of cations on their surfaces and within the space between the sheets. The presence of cations between the interlayer spaces results in unique physiochemical properties of clay minerals supporting certain applications while limiting the others [3]. Therefore, researchers are now focusing on the modifications of natural clay minerals to tune their properties for targeted applications. Different methods to modify the clay minerals including cations and anions exchange, organic and inorganic complexes, organic and inorganic anions binding, acid treatments, pillaring with poly cations, intra and interparticle polymerization, ultrasound, plasma, and physical treatments have been introduced [8]. For instance, Faiza and Gerhard [9] and Kumari and Mohan [10] modified the clay minerals by using a suitable pillaring agent to generate highly resistant, thermally stable, porous materials with large surface area. Therefore, modification of natural clay minerals to produce clay-based composites could have improved properties for targeted applications in environmental and industrial sectors. Hence, this chapter discusses the modification of natural clay minerals with various foreign materials to produce clay-based composites. Moreover, the new trends in the applications of clay composites in industry, agriculture, environment, and energy sector have been reviewed and discussed in this chapter.

2 Modification of Clay Minerals

Clay-based composites' development has gained a huge attention of researchers recently owing to their improved physiochemical properties and structural composition, consequently resulting in better performance as compared to the pristine natural clay minerals [2]. Clay minerals can be modified by following various methods such as calcination, magnetization, acid activation, and polymer or surfactant activation depending upon the target application [11–14]. In acid activation process, the Ca^{2+} in clay mineral is partially dissolved in acidic solution to replace Ca^{2+} with proton and to leach out Al^{3+}, Fe^{3+}, and Mg^{2+} from the silicate layer [15], whereas, in calcination process, the clay is treated thermally (high temperature) until certain level of heat for a specific period of time [16]. Likewise, magnetization is a process of pretreating the clay mineral with iron-based materials [11].

Combining the clay minerals with carbonaceous materials such as activated carbon and biochar is one of the most common method of clay modification. Moreover, combining clay minerals with organic compound has also been quite an interesting clay composite these days, as this type of clay composite has the hydrophobic and organofilic characteristics [17]. Combining synthetic silicate with the natural clay minerals results in the development of hybrid silicate–clay composite with improved stability and non-toxicity as compared to the pristine materials [18]. These non-toxic hybrid composites could be considered perfect candidates for the removal of dyes and heavy metal ions from the environment [2]. Therefore, clay minerals' modification and designing have gained much interest in recent times due to rapid industrialization and urbanization and gained a wide range of applications in agriculture, environment, energy, and industry sectors.

3 New Trends in the Application of Clay Composites

3.1 Application in the Environment

A rapid increase in population and industrialization has resulted in various environmental issues posing serious threats to the human health. The poisoning and degradation of the aquatic environment by numerous chemicals are one of modern society's key global challenges. Likewise, industrial effluents pose a substantial risk to drinking water sources, including heavy metal, organic and inorganic wastes, aromatic compounds, dyes, and so on. Therefore, for a sustainable environment and ecosystem, removal of toxic pollutants from different environmental matrices is of prime importance. Various technologies have been developed to remove contaminants from the environment; however, majority of the traditional technologies are either inefficient or expensive. Therefore, in order to take the next step toward a greener environment, researchers are in surge to develop cost-effective and environment-friendly materials to remove a range of environmental pollutants such as greases, inks, paints, rheological modifiers, pharmaceuticals, petrochemicals, and heavy metals [19]. Recently, removal of environmental contaminants using clay-based materials has gained much interest of the researchers.

Elevated levels of organic micropollutants in the environment is an emerging global concern [20]. The introduction of various natural and anthropogenic organic micropollutants in consort with other persistent contaminants is posing a serious health risk. Polycyclic aromatic hydrocarbons (PAHs) are persistent and pervasive organic micropollutants, which tend to accumulate in aquatic sediments due to their hydrophobic nature, which is a substantial health concerns for both human and aquatic life [21]. Various materials have been used for PAHs' degradation such as magnetic metal oxides–chitosan nanocomposites, graphene oxide, silver phosphate, and magnetic/graphene/chitosan nanocomposite. However, addition of clay-based materials into the removing agents could further enhance the flocculation process and result in better removal of the PAHs. For instance, Shabeer et al. [22] reported that combining clay minerals along with alum and poly aluminum chloride resulted in 37.4%–100.0% PAHs' removal, which was far better than using poly aluminum chloride and alum alone (20–38% PAHs' removal). Moreover, Cavallaro et al. [23] conducted a study and concluded that the toxicity of graphene oxide nanoplates in the aqueous phase could be substantially reduced by using planar kaolin clay.

Release and accumulation of heavy metals in various environmental compartments are another issue of the modern world. Heavy metals are released from industries, mining, vehicles, and agricultural activities, accumulate in the soil and water resources, and persist for longer period of times as these are non-degradable, subsequently deteriorating the health of ecosystem. For instance, Hg enters the water resources through many sources such as industrial activity, domestic effluents, and acid rain causing soil leaching. Likewise, Pb is introduced into the environment through industrial waste, automotive exhaust, incinerator ash, electronic wastes, and pesticides. Exposure to heavy metals may lead to cancer, renal and bone damage, breakdown of mucous membranes, and even impairment of production of progesterone and testosterone. Exposure to Hg has been linked to kidney, neurological system, and visual problems in humans, while Pb toxicity eventually leads to severe renal damage, anemia, hampered protein synthesis, and degeneration of the neurological system [19]. Therefore, it is need of the time to remove such dangerous heavy metals from environment on sustainable basis. Clay-based materials and their composites have been used by various researchers to remove heavy metals from the environment. For instance, Sundaram and Dharmalingam [24] synthesized magnetized polymer clay composites using bentonite, iron oxide, and monomer methyl methacrylate for the removal of Cr(VI) ions from contaminated water. The results revealed that the fabricated clay-based nanocomposite adsorbed 113 mg g^{-1} of Cr(VI) by following film diffusion and intraparticle diffusion mechanism [24]. In another work, organo-bentonite and polyacrylonitrile composites were synthesized and employed for the removal of heavy metals, and the results showed a maximum adsorption of 52.6, 65.4, and 77.4 mg g^{-1} for Cd(II), Zn(II), and Cu(II), respectively, at pH 6.0 by following ion exchange and metal chelation mechanisms [25]. Previously, chitosan–Al-pillared montmorillonite-based nanocomposite showed 96.0% and 99.5%, removal capacity for Cu (II) and Pb(II), respectively, at a pH of 6.5 by following chemisorption process [26]. The authors further stated that such clay-based nanocomposites had a stronger regeneration capacity. Wang et al. [27] have also used a similar kind of adsorbent (chitosan/montmorillonite nanocomposites) and observed its sorption capacity of 15.67 mg g^{-1} for Cr(VI). In another study, Msaadi et al. [28] synthesized ion-imprinted polymer/montmorillonite clay nanocomposite using a photopolymerization process and reported 301 mg g^{-1} of sorption capacity for Pb(II). In another study, nanocomposites were synthesized by using chitosan, methyl cellulose, and kaolin clay for the removal of Pb(II) ions [29]. The results revealed that application of nanochitosan/kaolin clay composites demonstrated 70% removal capacity for Pb(II) [29]. Therefore, clay-based composites can effectively be used for the efficient removal of heavy metals from the contaminated media.

Although much efforts have been exerted to develop efficient clay-based composites for the removal of organic and inorganic pollutants from the environment, there is still need to focus on developing cost-effective, greener, and consistently performing clay-based composites with mass production system. Moreover, fabricating clay-based nanosheets, nanotubes, and nanorods by exfoliation of clay minerals could produce highly efficient composite materials with larger surface area and more porosity.

3.2 Application in Agriculture

Due to unique characteristics of clay, the clay-based composites have various applications in agriculture sector including water conservation, nutrient retention, polluted soil remediation, wastewater treatment, and controlled-release fertilizers. Such composites can be used for effective water supply under water-stress circumstances, as well as for gradual and steady delivery of nutrients and insecticides contained in nanocarriers [30]. Thus, the uses of clay-based materials in agriculture sector have been discussed in this section.

3.2.1 Fertilizers

Inefficiency of chemical fertilizers is resulting in huge economic losses and environmental pollution. Therefore, the development of controlled-release fertilizers, superabsorbent, and membrane-encapsulated fertilizers could provide a slow and sustainable delivery of nutrients and can help to accomplish sustainable development goals. It was shown that traditional chemical fertilizers treated and encapsulated with polymers had a gradual and constant release of nutrients for longer periods of time as compared to untreated fertilizers, which released roughly 90% of the contained nutrients during the first five days [31]. The explanation for this rapid release was hypothesized to be the breakdown of nutrients from untreated chemical fertilizers in water, which resulted in a rapid release. However, in the case of encapsulated slow-release fertilizers, the nutrients absorbed in soil solution are said to be adsorbed on the surfaces of the polymers supplied and also imprisoned due to the polymers' high absorption capacity as superabsorbents. As a result, the absorbed and adsorbed nutrients in the soil solution are released slowly, acting as a gradual and consistent supply of nutrients for a longer length of time [30]. However, the type of substance utilized as an adsorbent influences the gradual and continuous release of nutrients.

Clay-based materials can be used as adsorbent agents in developing slow and controlled-release fertilizers. For instance, Sarkar et al. [32] investigated the impacts of polymers prepared from different types of clay (polymers synthesized from kaolinite, micaceous, and montmorillonite clays) on nutrient release and found that kaolinite clay-based materials showed the highest release of nutrients (90%) within 48 h of application, while montmorillonite clay-based materials released 70% of the nutrients. Furthermore, the nutrient release was discovered to be independent of amorphous aluminosilicate. Previously, it was reported that encapsulating fertilizers like urea with polymers and nanoclays to produce nanoclay–polymer composites could result in slower nitrogen release than uncoated urea, which resulted in 90% nitrogen release on the fifth day of application [33]. The authors further reported that only 61% of the nitrogen in encapsulated urea was released on the 30th day after application, suggesting a huge potential of nanosized clay composites in developing efficient controlled-release fertilizers.

3.2.2 Pesticides

For controlling pests in crops, nanocarriers have been utilized successfully because of their slow and steady delivery and effectiveness [34]. For slow and steady release of pesticides, two mechanisms, i.e., entrapment and encapsulation via weak ionic attachments are generally used. These processes could be accomplished by ensuring their anchorage with plant roots and rhizospheric soil, which subsequently provide protection and stability to environment by reducing runoff of chemicals, and reduction in environmental degradation process due to efficient absorption [35]. Therefore, nanoclay-encapsulated insecticides are more stable because they preserve the substance from degradation. Reduced premature degradation increased the availability of active components and decreased pesticide exposure to people and other living organisms, which leads to less pesticide consumption with more efficiency, resulting in environmental sustainability [36]. Alromeed et al. [37] synthesized a clay–gelatin-based composite of MCPA [(4-chloro-2-methylphenoxy) acetic acid] herbicide and demonstrated four-time decline in herbicide leaching with enhanced bioactivity as compared to commercial MCPA herbicide (used as control). Recent advancements in pesticide formulation have focused in developing pesticides with a gradual and continuous supply of active components due to enhanced solubility via microencapsulation [38]. However, the selection of encapsulating material is of critical importance, as it should be cheaper, non-toxic, and environment-friendly to ensure environmental sustainability [39–41].

3.3 Application in Biomedical

Due to environment-friendliness and safety, clay-based materials are ideal candidates for biomedical applications such as drug packaging and delivery, bone cementing, wound healing, tissue engineering, cancer therapy, and enzyme stabilization [42]. Thus, in this section, the most common applications of clay-based materials in biomedical sector have been discussed.

3.3.1 Pharmaceutical

Clay composites are being utilized in pharmaceutical, cosmetics, biomaterials, and biosensor production, as well as in several medical devices. Clay composites are widely being used to enhance the efficiency of drug as carrier and even as the active ingredient as to prevent any toxin, bacteria, and pathogens. For instance, Asthana et al. [43] cohol with montmorillonite clay and produced a skin ointment, which helps to reduce the appearance blemishes and redness and also combats allergic reactions caused by irritating lotions or cleansers. The authors further explained that the combination of aloe vera gel (hydrated) with montmorillonite clay has the ability to bind free radicals, bacteria, and toxins living on the surface of the skin and provides extra moisture to the skin [43]. Likewise, combining biomaterials with clay minerals can enhance the effectiveness of biomaterial for an efficient wound dressing in tissue engineering. For example, Bonifacio et al. [44] developed a hydrogel by combining glycerol and gellan gum with halloysite nanotubes for the purpose of soft tissue engineering (for regeneration of liver, skin, and pancreas). It was further reported that combining gellan gum with glycerol resulted in increased viscosity of the mixture, but halloysite nanotubes reduced water absorption by 30–35%. The addition of 5% halloysite nanotubes to chitosan/halloysite nanotube membranes increased mechanical qualities as well as thermal stability [45]. Likewise, Yu et al. [46] combined *Callicarpa nudiflora* (medicinal herb) with collagen and organo-montmorillonite to produce a composite membrane. The result showed that the combination of herb with the clay composite has a significant result in reducing bacterial activity by 70% as compared to the herb alone. In another study, Kapusetti et al. [47] produced cement/layered silicate nanohybrids with montmorillonite nanoclays to reduce cell necrosis and improve biocompatibility. Nanoclays' composites with polymethyl methacrylate, which is a bone cementing agent, strengthen and enhance the efficiency for bone cementing and bone implant applications with improved biological characteristics and mechanical strength [48]. Moreover, due to their implication as filler material, nanoclays' application along with hydrogels improves the propagation and adhesion of cells and helps in desired tuning and restoration of tissue functionalities [49].

Clay composite's wound healing applications have also been extensively researched in order to minimize pain, infection, and to enhance scar resistant and wound dressing in healing wounds [50–52]. Properties of clays such as flexibility and swelling are crucial in this context. Sabaa et al. [53] reported that a biodegradable polyvinyl alcohol composite containing carboxymethyl chitosan and montmorillonite demonstrated a greater swelling behavior and high antibacterial efficacy. Alike, a composite of polyvinyl alcohol and Iranian gum tragacanth containing kaolinite-based nanoclays has shown increased mechanical and chemical properties, demonstrating an efficient material for wound healing [54]. In nutshell, natural aluminosilicate clays along with their biodegradable composite proved non-toxic, biocompatible, and pH sensitive in drug delivery systems and possessed excellent stretching, filling, and healing properties in application for bone cementing, tissue engineering, and wound healing. Therefore, clay-based composite materials are being produced and effectively employed for various purposes in pharmaceutical industry.

3.3.2 Drug Delivery

Clay-based composites have also been used in drug delivery applications for anti-inflammatories, antibiotics, antimicrobial, antihistamines, antialgal, antifungal, and anticancer therapies [55–63]. As the drug release is controlled in intercalated layered materials, application of such novel materials in the pharmaceutical sector has a great potential. The presence of clay in medicines can control the rate of drug release and thereby improves the dissolution of drug subsequently ensuring that the drugs have effectively reached the specific organ without affecting other organ in the body [64]. Tipa et al. [65] prepared polymer–clay composites based on pluronics and nanoclays with a 2 wt% addition of clay and observed a long-term drug delivery profile of up to 45 days.

Mura et al. [66] studied various kinds of clays including bentonite, attapulgite, and sepiolite together to govern release and dissolution behavior of oxaprozin (an anti-inflammatory drug) and found sepiolite with best performance in enhancing therapeutic effectiveness. Likewise, Roozbahani et al. [61] reported that laponite nanoplatelets can efficiently be used for controlled and persistent release of anionic dexamethasone via encapsulation inside the interlayer space of laponite nanodisks. Zeynabad et al. [67] reported that an organo-modified laponite–polymer composite nanoclay enhanced the encapsulation effectiveness by 90% for a dual drug delivery system which depends on pH for cancer treatment. It has been established that the application of nanoclays serves as an efficient and useful strategy to enhance the therapeutic efficacy of less-soluble medicines such as oxyproline and cyclodextrin, subsequently reducing the quantities of such medications [42]. Tabasi et al. [68] used clay ceramics as nanocarrier and tried to explain the higher capacity of such materials for carrying drugs. In this research, nanoclay demonstrated remarkable potential in nanovaccine technology that can be used to prevent tumor growth and various infectious diseases such as COVID-19, influenza, pathogenic Escherichia coli (*E. coli*), and Leptospira.

3.4 Application in Industry

Clays are the oldest and perhaps one of the most interesting and versatile materials [69]. Unique properties of clays make them suitable for various industrial applications. Clays are becoming more and more popular today thanks to their intriguing characteristics, which include natural abundance, affordable prices, stability, and compatibility [70]. Clays are extremely adaptable and very affordable materials for the creation of sophisticated clay composites due to their rich intercalation chemistry, distinctive layered structure, high aspect ratio, and excellent in-plane strength and stiffness [69]. Clay-based composite materials have also been effectively used in energy generation and storage purposes. The utilization of clay composites in the energy industry may be characterized by (i) increased safety, (ii) increased comfort, (iii) lighter vehicles that save fuel and decrease CO_2 emissions, and (iv) improved drivability [19]. Higher surface area and porosity are the most important factors to enhance thermal energy storage capacity. In this scenario, clay-based composites are of significant importance for energy storage purpose owing to their higher porosity and larger surface area [71]. Musyoka and Langmi [71] stated that the water-saturated clay minerals are efficient materials for underground storage of solar energy for longer period of time. Likewise, by Gabrielsson et al. (1997) [72] reported that soft clay can effectively store thermal energy even at 70 °C of temperature.

It has been established that the additive manufacturing, often known as three-dimensional (3D) printing, can potentially transform numerous industries; however, the wide-ranging effects of 3D printing on water treatment membranes are not understood. The most common 3D printing plastics used are chlorinated polyethylene, acrylonitrile butadiene styrene, and polylactic acid, which are durable but bit expensive [73]. Therefore, if combined with nanoclays, the usage of polypropylene in the form of plastic in various ratios to manufacture 3D filaments can be achieved with more efficiently as it is cheaper and cellulosis plastic, which is used as a softwood pulp [74]. Moreover, Youmoue et al. [75] stated that using sawdust as a porogen agent, clay-based ceramic composite materials with hydraulic permeability can be used as promising candidates for microfiltration. Therefore, based on the targeted application in industry, natural clay minerals can be appropriately modified to achieve efficient, cost-effective, and environment-friendly composite materials.

4 Conclusion

Natural clay minerals are cost-effective, abundant, and environment-friendly materials and are widely being used in various industrial and agricultural sectors. However, the crystal structure and negative charges on surface make then efficient materials for specific applications. Therefore, modifying the natural clay minerals with foreign materials to produce clay composite has gained much attention of the researchers recently. These modifications result in improved surface area, porosity, and other characteristics of the clay-based composite, making them suitable for variety of applications. Clay-based composites have widely been employed in agriculture sector (fertilizer and pesticides), environment (soil remediation and rehabilitation as well as wastewater treatment), industries, energy storage devices, and biomedical applications (pharmaceuticals and drug delivery). Future research should focus on developing the most efficient and low-cost modification techniques to design clay-based composites for versatile application. Moreover, new modification techniques should be explored to produce large-scale clay-based composites with consistent properties.

References

1. Uddin, M.K.: A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. Chem. Eng. J. **308**, 438–462 (2017)
2. Han, H., Rafiq, M.K., Zhou, T., Xu, R., Mašek, O., Li, X.: A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants. J. Hazard. Mater. **369**, 780–796 (2019)
3. Otunola, B.O., Ololade, O.O.: A review on the application of clay minerals as heavy metal adsorbents for remediation purposes. Environ. Technol. Innov. **18**, 100692 (2020)
4. Xi, Y., Mallavarapu, M., Naidu, R.: Preparation, characterization of surfactants modified clay minerals and nitrate adsorption. Appl. Clay Sci. **48**(1–2), 92–96 (2010)
5. España, V.A.A., Sarkar, B., Biswas, B., Rusmin, R., Naidu, R.: Environmental applications of thermally modified and acid activated clay minerals: current status of the art. Environ. Technol. Innov. **13**, 383–397 (2019)
6. Toor, M., Jin, B.: Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing diazo dye. Chem. Eng. J. **187**, 79–88 (2012)
7. Vimonses, V., Lei, S., Jin, B., Chow, C.W., Saint, C.: Adsorption of congo red by three Australian kaolins. Appl. Clay Sci. **43**(3–4), 465–472 (2009)
8. Arfaoui, S., Frini-Srasra, N., Srasra, E.: Modelling of the adsorption of the chromium ion by modified clays. Desalination **222**(1–3), 474–481 (2008)
9. Faiza, B., Gerhard, L.: Surface modification of clay minerals. Appl. Clay Sci. **19**(1), 3 (2001)
10. Kumari, N., Mohan, C.: Basics of clay minerals and their characteristic properties. Clay Clay Miner. **24**, 1–29 (2021)
11. Cottet, L., Almeida, C.A.P., Naidek, N., Viante, M.F., Lopes, M.C., Debacher, N.A.: Adsorption characteristics of montmorillonite clay modified with iron oxide with respect to methylene blue in aqueous media. Appl. Clay Sci. **95**, 25–31 (2014). https://doi.org/10.1016/j.clay.2014.03.023
12. El Mouzdahir, Y., Elmchaouri, A., Mahboub, R., Gil, A., Korili, S.A.: Equilibrium modeling for the adsorption of methylene blue from aqueous solutions on activated clay minerals. Desalination **250**(1), 335–338 (2010)
13. Kahraman, H.T.: Development of an adsorbent via chitosan nano-organoclay assembly to remove hexavalent chromium from wastewater. Int. J. Biol. Macromol. **94**, 202–209 (2017)

14. Pentrák, M., Czímerová, A., Madejová, J., Komadel, P.: Changes in layer charge of clay minerals upon acid treatment as obtained from their interactions with methylene blue. Appl. Clay Sci. **55**, 100–107 (2012)
15. Carrado, K.A., Komadel, P.: Acid activation of bentonites and polymer-clay nanocomposites. Elements **5**(2), 111–116 (2009)
16. Taylor-Lange, S.C., Lamon, E.L., Riding, K.A., Juenger, M.C.G.: Calcined kaolinite–bentonite clay blends as supplementary cementitious materials. Appl. Clay Sci. **108**, 84–93 (2015)
17. Jia, S., Yang, Z., Ren, K., Tian, Z., Dong, C., Ma, R., Yu, G., Yang, W.: Removal of antibiotics from water in the coexistence of suspended particles and natural organic matters using amino-acid-modified-chitosan flocculants: a combined experimental and theoretical study. J. Hazard. Mater. **317**, 593–601 (2016)
18. Wang, W., Tian, G., Zhang, Z., Wang, A.: A simple hydrothermal approach to modify palygorskite for high-efficient adsorption of Methylene blue and Cu (II) ions. Chem. Eng. J. **265**, 228–238 (2015)
19. Ali, F., Ullah, H., Ali, Z., Rahim, F., Khan, F., Rehman, Z.U.: Polymer-clay nanocomposites, preparations and current applications: a review. Curr. Nanomater. **1**(2), 83–95 (2016)
20. Ahmad, J., Naeem, S., Ahmad, M., Usman, A.R., Al-Wabel, M.I.: A critical review on organic micropollutants contamination in wastewater and removal through carbon nanotubes. J. Environ. Manage. **246**, 214–228 (2019)
21. Munyengabe, A., Ndibewu, P.P., Sibali, L.L., Ngobeni, P.: Polymeric nanocomposite materials for photocatalytic detoxification of polycyclic aromatic hydrocarbons in aquatic environments—a review. Results Eng. 100530 (2022)
22. Shabeer, T.A., Saha, A., Gajbhiye, V.T., Gupta, S., Manjaiah, K.M., Varghese, E.: Removal of poly aromatic hydrocarbons (PAHs) from water: effect of nano and modified nano-clays as a flocculation aid and adsorbent in coagulation-flocculation process. Polycyclic Aromat. Compd. **34**(4), 452–467 (2014)
23. Cavallaro, G., Lazzara, G., Rozhina, E., Konnova, S., Kryuchkova, M., Khaertdinov, N., Fakhrullin, R.: Organic-nanoclay composite materials as removal agents for environmental decontamination. RSC Adv. **9**(69), 40553–40564 (2019)
24. Sundaram, E.S., Dharmalingam, P.: Synthesis and characterization of magnetized clay polymer nanocomposites and its adsorptive behaviour in removal of Cr (VI) from aqueous phase. Asian J. Chem. **30**, 667–672 (2018)
25. Anirudhan, T.S., Ramachandran, M.: Synthesis and characterization of amidoximated polyacrylonitrile/organobentonite composite for Cu (II), Zn (II), and Cd (II) adsorption from aqueous solutions and industry wastewaters. Ind. Eng. Chem. Res. **47**(16), 6175–6184 (2008)
26. Duan, L., Hu, N., Wang, T., Wang, H., Ling, L., Sun, Y., Xie, X.: Removal of copper and lead from aqueous solution by adsorption onto cross-linked chitosan/montmorillonite nanocomposites in the presence of hydroxyl–aluminum oligomeric cations: equilibrium, kinetic, and thermodynamic studies. Chem. Eng. Commun. **203**(1), 28–36 (2016)
27. Wang, Y.M., Duan, L., Sun, Y., Hu, N., Gao, J.Y., Wang, H., Xie, X.M.: Adsorptive removal of Cr (VI) from aqueous solutions with an effective adsorbent: cross-linked chitosan/montmorillonite nanocomposites in the presence of hydroxy-aluminum oligomeric cations. Desalin. Water Treat. **57**(23), 10767–10775 (2016)
28. Msaadi, R., Ammar, S., Chehimi, M.M., Yagci, Y.: Diazonium-based ion-imprinted polymer/clay nanocomposite for the selective extraction of lead (II) ions in aqueous media. Eur. Polymer J. **89**, 367–380 (2017)
29. Kanchana, V., Gomathi, T., Geetha, V., Sudha, P.N.: Adsorption analysis of Pb (II) by nanocomposites of chitosan with methyl cellulose and clay. Pharm. Lett. **4**(4), 1071–1079 (2012)
30. Ditta, A.: Role of nanoclay polymers in agriculture: Applications and perspectives. In: Nanohybrids in Environmental & Biomedical Applications, pp. 323–334. CRC Press (2019)
31. Wu, L., Liu, M., Liang, R.: Preparation and properties of a double-coated slow-release NPK compound fertilizer with superabsorbent and water-retention. Biores. Technol. **99**(3), 547–554 (2008)

32. Sarkar, S., Datta, S.C., Biswas, D.R.: Synthesis and characterization of nanoclay–polymer composites from soil clay with respect to their water-holding capacities and nutrient-release behavior. J. Appl. Polym. Sci. **131**(6) (2014)
33. Guo, M., Liu, M., Zhan, F., Wu, L.: Preparation and properties of a slow-release membrane-encapsulated urea fertilizer with superabsorbent and moisture preservation. Ind. Eng. Chem. Res. **44**(12), 4206–4211 (2005)
34. Khot, L.R., Sankaran, S., Maja, J.M., Ehsani, R., Schuster, E.W.: Applications of nanomaterials in agricultural production and crop protection: a review. Crop Prot. **35**, 64–70 (2012)
35. Johnston, C.T.: Probing the nanoscale architecture of clay minerals. Clay Miner. **45**(3), 245–279 (2010)
36. Nuruzzaman, M.D., Rahman, M.M., Liu, Y., Naidu, R.: Nanoencapsulation, nano-guard for pesticides: a new window for safe application. J. Agric. Food Chem. **64**(7), 1447–1483 (2016)
37. Alromeed, A.A., Scrano, L., Bufo, A., S. and Undabeytia, T.: Slow-release formulations of the herbicide MCPA by using clay–protein composites. Pest Manage. Sci. **71**(9), 1303–1310 (2015)
38. Gouin, S.: Microencapsulation: industrial appraisal of existing technologies and trends. Trends Food Sci. Technol. **15**(7–8), 330–347 (2004)
39. de Oliveira, J.L., Campos, E.V.R., Bakshi, M., Abhilash, P.C., Fraceto, L.F.: Application of nanotechnology for the encapsulation of botanical insecticides for sustainable agriculture: prospects and promises. Biotechnol. Adv. **32**(8), 1550–1561 (2014)
40. Grillo, R., Abhilash, P.C., Fraceto, L.F.: Nanotechnology applied to bio-encapsulation of pesticides. J. Nanosci. Nanotechnol. **16**(1), 1231–1234 (2016)
41. Kah, M., Hofmann, T.: Nanopesticide research: current trends and future priorities. Environ. Int. **63**, 224–235 (2014)
42. Peña-Parás, L., Sánchez-Fernández, J.A., Vidaltamayo, R.: Nanoclays for biomedical applications. Handb. Ecomater. **5**, 3453–3471 (2018)
43. Asthana, N., Pal, K., Aljabali, A.A., Tambuwala, M.M., de Souza, F.G., Pandey, K.: Polyvinyl alcohol (PVA) mixed green–clay and aloe vera based polymeric membrane optimization: peel-off mask formulation for skin care cosmeceuticals in green nanotechnology. J. Mol. Struct. **1229**, 129592 (2021)
44. Bonifacio, M.A., Gentile, P., Ferreira, A.M., Cometa, S., De Giglio, E.: Insight into halloysite nanotubes-loaded gellan gum hydrogels for soft tissue engineering applications. Carbohyd. Polym. **163**, 280–291 (2017)
45. De Silva, R.T., Pasbakhsh, P., Goh, K.L., Chai, S.P., Ismail, H.J.P.T.: Physico-chemical characterisation of chitosan/halloysite composite membranes. Polym. Testing **32**(2), 265–271 (2013)
46. Yu, X., Guo, L., Liu, M., Cao, X., Shang, S., Liu, Z., Huang, D., Cao, Y., Cui, F., Tian, L.: Callicarpa nudiflora loaded on chitosan-collagen/organomontmorillonite composite membrane for antibacterial activity of wound dressing. Int. J. Biol. Macromol. **120**, 2279–2284 (2018)
47. Kapusetti, G., Misra, N., Singh, V., Srivastava, S., Roy, P., Dana, K., Maiti, P.: Bone cement based nanohybrid as a super biomaterial for bone healing. J. Mater. Chem. B **2**(25), 3984–3997 (2014)
48. Al Thaher, Y., Perni, S., Prokopovich, P.: Nano-carrier based drug delivery systems for sustained antimicrobial agent release from orthopaedic cementous material. Adv. Coll. Interface Sci. **249**, 234–247 (2017)
49. Zafar, R., Zia, K.M., Tabasum, S., Jabeen, F., Noreen, A., Zuber, M.: Polysaccharide based bionanocomposites, properties and applications: a review. Int. J. Biol. Macromol. **92**, 1012–1024 (2016)
50. Noori, S., Kokabi, M., Hassan, Z.M.: Nanoclay enhanced the mechanical properties of poly (vinyl alcohol)/chitosan/montmorillonite nanocomposite hydrogel as wound dressing. Proc. Mater. Sci. **11**, 152–156 (2015)
51. Sandri, G., Aguzzi, C., Rossi, S., Bonferoni, M.C., Bruni, G., Boselli, C., Cornaglia, A.I., Riva, F., Viseras, C., Caramella, C., Ferrari, F.: Halloysite and chitosan oligosaccharide nanocomposite for wound healing. Acta Biomater. **57**, 216–224 (2017)

52. Yang, C., Xue, R., Zhang, Q., Yang, S., Liu, P., Chen, L., Wang, K., Zhang, X., Wei, Y.: Nanoclay cross-linked semi-IPN silk sericin/poly (NIPAm/LMSH) nanocomposite hydrogel: an outstanding antibacterial wound dressing. Mater. Sci. Eng. C **81**, 303–313 (2017)
53. Sabaa, M.W., Abdallah, H.M., Mohamed, N.A., Mohamed, R.R.: Synthesis, characterization and application of biodegradable crosslinked carboxymethyl chitosan/poly (vinyl alcohol) clay nanocomposites. Mater. Sci. Eng. C **56**, 363–373 (2015)
54. Heydary, H.A., Karamian, E., Poorazizi, E., Khandan, A., Heydaripour, J.: A novel nano-fiber of Iranian gum tragacanth-polyvinyl alcohol/nanoclay composite for wound healing applications. Proc. Mater. Sci. **11**, 176–182 (2015)
55. Fizir, M., Dramou, P., Zhang, K., Sun, C., Pham-Huy, C., He, H.: Polymer grafted-magnetic halloysite nanotube for controlled and sustained release of cationic drug. J. Colloid Interface Sci. **505**, 476–488 (2017)
56. Jayrajsinh, S., Shankar, G., Agrawal, Y.K., Bakre, L.: Montmorillonite nanoclay as a multifaceted drug-delivery carrier: a review. J. Drug Deliv. Sci. Technol. **39**, 200–209 (2017)
57. Jiang, W.T., Chang, P.H., Tsai, Y., Li, Z.: Halloysite nanotubes as a carrier for the uptake of selected pharmaceuticals. Microporous Mesoporous Mater. **220**, 298–307 (2016)
58. Karnik, S., Jammalamadaka, U.M., Tappa, K.K., Giorno, R., Mills, D.K.: Performance evaluation of nanoclay enriched anti-microbial hydrogels for biomedical applications. Heliyon **2**(2), e00072 (2016)
59. Li, X., Ouyang, J., Yang, H., Chang, S.: Chitosan modified halloysite nanotubes as emerging porous microspheres for drug carrier. Appl. Clay Sci. **126**, 306–312 (2016)
60. Massaro, M., Amorati, R., Cavallaro, G., Guernelli, S., Lazzara, G., Milioto, S., Noto, R., Poma, P., Riela, S.: Direct chemical grafted curcumin on halloysite nanotubes as dual-responsive prodrug for pharmacological applications. Colloids Surf. B **140**, 505–513 (2016)
61. Roozbahani, M., Kharaziha, M., Emadi, R.: pH sensitive dexamethasone encapsulated laponite nanoplatelets: release mechanism and cytotoxicity. Int. J. Pharm. **518**(1–2), 312–319 (2017)
62. Wang, X., Du, Y., Luo, J., Lin, B., Kennedy, J.F.: Chitosan/organic rectorite nanocomposite films: structure, characteristic and drug delivery behaviour. Carbohyd. Polym. **69**(1), 41–49 (2007)
63. Yang, J.H., Lee, J.H., Ryu, H.J., Elzatahry, A.A., Alothman, Z.A., Choy, J.H.: Drug–clay nanohybrids as sustained delivery systems. Appl. Clay Sci. **130**, 20–32 (2016)
64. Sangeetha, K., Angelin Vinodhini, P., Sudha, P.N.: Clay based biopolymer nanocomposites and their applications in environmental and biomedical fields. In: Inamuddin, S.T., Mishra, R.K., Asiri, A.M. (Eds.) Sustainable Polymer Composites and Nanocomposites, pp. 1159–1183. Springer International Publishing, Cham (2019)
65. Tipa, C., Cidade, M.T., Vieira, T., Silva, J.C., Soares, P.I., Borges, J.P.: A new long-term composite drug delivery system based on thermo-responsive hydrogel and nanoclay. Nanomaterials **11**(1), 25 (2020)
66. Mura, P., Maestrelli, F., Aguzzi, C., Viseras, C.: Hybrid systems based on "drug–in cyclodextrin–in nanoclays" for improving oxaprozin dissolution properties. Int. J. Pharm. **509**(1–2), 8–15 (2016)
67. Zeynabad, F.B., Salehi, R., Mahkam, M.: Design of pH-responsive antimicrobial nanocomposite as dual drug delivery system for tumor therapy. Appl. Clay Sci. **141**, 23–35 (2017)
68. Tabasi, H., Oroojalian, F., Darroudi, M.: Green clay ceramics as potential nanovehicles for drug delivery applications. Ceram. Int. **47**(22), 31042–31053 (2021)
69. Ray, S.S.: Recent trends and future outlooks in the field of clay-containing polymer nanocomposites. Macromol. Chem. Phys. **215**(12), 1162–1179 (2014)
70. Sabouri, Z., Fereydouni, N., Akbari, A., Hosseini, H.A., Hashemzadeh, A., Amiri, M.S., Kazemi Oskuee, R., Darroudi, M.: Plant-based synthesis of NiO nanoparticles using salvia macrosiphon Boiss extract and examination of their water treatment. Rare Met. **39**(10), 1134–1144 (2020)
71. Musyoka, N.M., Langmi, H.W.: Clay and clay-supported materials for clean energy storage applications. Bentonite: Characteristics, Uses and Implications for the Environment. New York, USA, Nova Publishers (2015)

72. Gabrielsson, A., Lehtmets, M., Moritz, L., Bergdahl, U.: Heat storage in soft clay. Field tests with heating (70 C) and freezing of the soil. Statens geotekniska institute (1997)
73. Lackner, M.: Bioplastics Kirk-Othmer Encyclopedia of Chemical Technology, pp. 1–41 (2015)
74. Abdelaal, O.A., Darwish, S.M.: Review of rapid prototyping techniques for tissue engineering scaffolds fabrication. In: Öchsner, A., Silva, L.F., Altenbach, H. (eds.) Characterization and Development of Biosystems and Biomaterials, pp. 33–54. Springer, Berlin Heidelberg, Berlin (2013)
75. Youmoue, M., Fongang, R.T., Sofack, J.C., Kamseu, E., Melo, U.C., Tonle, I.K., Leonelli, C., Rossignol, S.: Design of ceramic filters using Clay/Sawdust composites: effect of pore network on the hydraulic permeability. Ceram. Int. **43**(5), 4496–4507 (2017)

Clay-Biochar Composites

Synthesis and Characterization of Clay-Biochar Composites

Mutair A. Akanji, Hamed A. Al-Swadi, Mohammed Awad Mousa Mousa,
Muhammad Usama, Munir Ahmad, Nahrir M. A. Lubis,
Abdullah S. F. Al-Farraj, and Mohammad I. Al-Wabel

Abstract Clay minerals have gained a huge attention of the researcher in recent years owing to their widespread applications in environment, agriculture, industry, and pharmacy. Despite of the unique properties of clay, there are some limitations in agricultural and environmental applications of clays, which includes removing hydrophobic organic micropollutants, utilization of fixed-bed media and in flocculation water treatment. Therefore, several researchers have attempted to fabricate clay-based composites with other materials such as biochar to improve and tune the properties of clays for targeted applications. Biochar is produced from the pyrolysis of waste materials and is characterized by a negative surface charge, larger surface area, numerous surface functional groups, high cationic exchange capacity, higher recalcitrance, and large pore volume. Therefore, synthesis of clay–biochar composites via surface, chemical, mechanical, or physical modifications could generate efficient materials with improved characteristics for specific applications. Thus, the techniques to synthesize clay–biochar composites for various applications are reviewed and discussed in this chapter. The variations in the chemical, physical, surface, and structural characteristics of clay–biochar composites are also discussed. Moreover, efficient, cost-effective, and environment-friendly technologies to synthesize clay–biochar composites are highlighted, and new emerging applications are recommended.

Keywords Engineered materials · Intercalation · Environmental pollution · Surface modifications · Remediation

---

M. A. Akanji · H. A. Al-Swadi · M. A. Mousa Mousa · M. Usama · M. Ahmad · N. M. A. Lubis · A. S. F. Al-Farraj · M. I. Al-Wabel (✉)
Soil Sciences Department, College of Food & Agricultural Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia
e-mail: malwabel@ksu.edu.sa

Department of Soil, Water and Environment, Faculty of Agriculture, Food and Environment, Sana'a University, Sana'a, Yemen

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_5

1 Introduction to Clay-Biochar Composites

In a controlled process known as pyrolysis, organic waste from forestry and agricultural operations is burnt to produce biochar, a material that resembles charcoal. Although it resembles regular charcoal in appearance, biochar is created using a particular procedure to lessen contamination and conserving carbon. In the process of pyrolysis, organic materials like wood and plants are burnt in an environment with limited oxygen. The substances burn with minimal to no harmful gas emissions. The organic material is turned into biochar during the pyrolysis process, a stable carbon form that would be hard to release into the atmosphere. Heat or energy produced by pyrolysis can be captured and used to generate clean energy. When it comes to stabilizing carbon, biochar is by far more effective and cleaner than other types of charcoal. Biochar made by the pyrolysis of biomass in the conditions of no or little oxygen is in fact carbon-rich charcoal [1, 2]. Biochar can have many applications such as environmental remediation [3]. This is as a result of its many functional groups on the surface, negative surface charge, as well as additional structural and textural characteristics like high porosity, large specific surface area, and substantial cation exchange capacity. These characteristics make biochar extremely effective in binding both organic and inorganic pollutants [4]. The sorts of raw materials that are generally easily accessible as waste materials have an impact on the physicochemical characteristics of biochar. A few factors affecting the charcoal pyrolysis process are temperature, heating rate, residence time, and reactor type [5]. It is well known that biochar has highly developed pores [6, 7], many functional groups [8] numerous inorganic nutrients [9], and very stable carbon [10]. Consequently, biochar has a variety of uses, including enhancing soil fertility [11], contaminants immobilization [12, 13], treatment of wastewater [14, 15], exhaust gas treatment [16] as well as in-place carbon storage. Sustainable waste management is indirectly supported by the utilization of biomass as a raw material to create biochar.

Biochar activation or modification increases its physicochemical qualities even though unaltered biochar has demonstrated great performance in environmental applications [8]. There have been various attempts to activate biochar without the use of outside doping agents by using steam, gas, oxidants, and acids [17]. Engineered biochar is a prospective contender for a variety of environmental uses, including enhancement of soil fertility, immobilization of contaminants, and treatment of wastewater. Another way is the modification of biochar with other materials such as clay to enhance the properties of the biochar and results in a substance called clay-biochar composite.

One of the world's richest natural resources is clay. Although clay is widely used for various purposes, such as an adsorbent, however, various applications are strongly dependent on its structural and chemical composition, which determines its chemical and physical qualities [18]. Clays come in a variety of forms, but they are all distinguished by having a lot of surface hydroxyl groups, high cation exchange capacity, and good stability [1, 2]. These characteristics increase their potential for adsorption.

However, clay can be combined with other materials to enhance its adsorbent qualities. In light of this, clay-biochar composites made from biomass waste and biochar have been developed [18–23].

The ongoing green and sustainable remediation movement is in line with biochar that has been amended with clay minerals. Clay-biochar composite holds a great potential because it has numerous uses in both agriculture and environmental cleanup. The physical characteristics and chemical fertility of soil are immediately improved using various biochar composites and thus increase agricultural output. However, environmental-friendly and sustainable methods of soil remediation will require the development of new materials in the future [24]. Clay-biochar composites have been created in numerous experiments and utilized to remove a variety of contaminants, including methylene blue, cadmium, and arsenic [18]. In this chapter, novel trends of clay-biochar synthesis are identified and assessed critically.

Although only a few studies have examined the production processes and environmental applications of clay-biochar composites, it is still difficult to identify new patterns in the synthesis of this material. The goal of this chapter is to classify and characterize clay-biochar composites while also discussing the factors that lead to their production. Additionally, the necessity of clay-biochar composites will be explored, along with how to best tailor them to the intended use.

2 Need to Synthesize Clay-Biochar Composites

The Amazonians first discovered the benefits of biochar thousands of years ago when organic and agricultural waste were burnt and buried. We can still benefit from these advantages using modern science [25]. Here are a few advantages of biochar: It can assist in restoring deficient soil, it lessens waste by devising an effective method of recycling organic material; it serves as a carbon sink since the production of biochar from biomass produces less carbon dioxide than burning biomass; heavy metals from the soil can be absorbed by it; it raises the pH of the soil to make it less acidic; and also acts as a natural habitat for microorganisms that improve the soil's quality, allowing plants to thrive where they couldn't before.

Despite all the benefits of biochar, it has some limitations that need to be aware of when using it. These incudes compacting of the soil as a result of regular biochar treatment, hence, negatively impacting crop yield; it can limit the activity of earthworms in the soil which are essential for plant health, as they improve nutrient cycling, increase soil aeration, and promote better plant growth; although it increases crop production but it absorbs some of the useful nutrients in the soil and as a result, it decreases the nutrients available for the plants; it can absorb pesticides when applied to the soil and thus negatively impacting their effect; it can affect soil's vulnerability with respect to harsh weather conditions. In order to fix those issues, combining clay minerals, a natural product with biochar, might improve the flaws and issues that arise from using biochar alone by altering the final product's chemistry and physical makeup.

In recent years, as an effective low-cost adsorbent for environmental applications, unique engineered biochar containing clay minerals dispersed on carbon surfaces inside the biochar matrix has been developed. Clay minerals have a variety of physical and chemical traits that increase the effectiveness of biochar when combined with it to form a composite. Clay minerals are frequently used in industrial engineering, agriculture, and petroleum refining. Clay minerals possess a number of valuable physical and chemical characteristics including surface chemistry, particle shape, exchange capacity, lamellar structure, functional group, and surface area [26]. Heavy metals, dyes, and organic molecules, among other contaminants, can be effectively fixed by clay minerals [27]. The clay minerals (kaolinite and montmorillonite) have received ample attention because they have the potential to be employed as inexpensive adsorbents.

As an adsorbent, clay-biochar composites have many benefits, including being economical, simple to use, and environmentally benign. Biochar can be made from a variety of precursors, many of which are readily available, and it has a higher adsorption capacity than other common adsorbents. Many studies have shown that engineered biochar, which is made from two inexpensive resources (clay and biochar), is an effective adsorbent for removing pollutants from the environment, such as heavy metals.

3 Techniques to Synthesize Clay-Biochar Composites

Clay-biochar composites have been synthesized with different techniques to suit their target application. There is variation in the ratio of biomass to clay or biochar to clay preparation. Also, the pyrolysis temperature varies resulting in different characteristics and properties of the produced composite. One of the techniques employed in synthesizing clay-biochar composite involves mixing the biomass and clay before pyrolyzis as seen in the production of montmorillonite and red earth–biochar composite by Premarathna et al. [23]. Here, 50 g clay was added to 2 L of deionized water and then sonicated with an ultrasonicator for 30 min, after which 250 g of feedstock (municipal solid waste) was added to the clay suspension and then shaken for 2 h with a mechanical shaker to ensure homogeneity of the mixture. The clay-feedstock suspension was filtered from the liquid and oven-dried to remove the moisture after which it was subjected to pyrolysis (at 500 °C for 30 min) in a little amount of oxygen. The produced clay-biochar composite materials were thoroughly washed with deionized water to get rid of any soluble contaminants. A similar technique was practiced by Ismadji et al. [18] for the production of bentonite hydrochar composite though there were little modification. In this procedure, the clay to feedstock ratio was 1:2 (25 g of bentonite powder and 50 g of cassava peel powder). Also, the pyrolysis time was 1 h under the flow of nitrogen for some part of the pyrolysis period. Similarly, in a study by Rawal et al. [28] where iron-clay-biochar composite was produced, the clay minerals and biomass were mixed before pyrolysis. In this study, kaolinite and bentonite were the clay minerals, while bamboo was used as the feedstock with different pyrolysis temperature (250 °C, 350 °C, 450 °C, and 550 °C) for 30 min. Furthermore, Fosso-Kankeu et al. [20] produced bentonite–biochar composite from the pyrolysis of a mixture of bentonite and sweet sorghum bagasse (mass ratio of 1:5) at a pyrolysis temperature of 400 °C in the presence nitrogen. Similarly, Borthakur et al. [19] synthesized montmorillonite and red earth–biochar composite by pyrolyzing a mixture of municipal solid waste with montmorillonite and natural red earth at 500 °C for 30 min under an oxygen-less environment. Here, 50 g of each of the montmorillonite and natural red earth and 250 g of the feedstock in 2 L deionized water were mixed and shaken for 2 h. Filtered clay-feedstock suspensions were dried in an oven overnight at 80 °C before being pyrolyzed at the aforementioned temperature to produce the composite. In a similar technique where pyrolysis was done after mixing biomass with clay, Chen et al. [29] produced attapulgite-clay-biochar composite following the pyrolysis of attapulgite and bagasse mixture. In this study, 4 g of attapulgite was mixed with 20 g of bagasse in a beaker after which 50 ml of deionized water was added and the mixture was made into paste by stirring it vigorously with a magnetic stirrer. The paste was then ground into powder after being oven-dried at 105 °C. The dried substance was then subjected to pyrolysis using a muffle furnace in an argon atmosphere at 700 °C for 4 h. The produced composite was washed severally with deionized water and then oven-dried. Similarly, a composite of attapulgite-clay and biochar was made by Yao et al. [30] following the technique stated by Li et al. [31]. Here, firstly, a stable suspension of attapulgite was made by mixing 2 g of attapulgite powder with 80 ml of deionized water, then ultrasonically sonicating the mixture for 30 min. Following that, 10 g of the biomass was added to the attapulgite suspensions and mixed by stirring for two hours. The biomass was then removed from the mixture and dried in an oven at 80 °C. The attapulgite treated biomass feedstocks were then pyrolyzed under oxygen-limited environment using a muffle furnace with a pyrolysis temperature of 500 °C for a period of 6 h to produce the composite. Likewise, biochar-montmorillonite composites were produced from the pyrolysis of a mixture of biomass (cauliflower leaves) and montmorillonite clay with a pyrolysis temperature of 500 °C for a period of 6 h [32].

Another technique is pyrolyzing the feedstock before mixing it with the clay mineral to form composite. For example, MgAl-LDH (Layered Double Hydroxide)/biochar composite was produced by Meili et al. [4] by adopting the co-precipitation in accordance with Zhang et al. [33]. Here, 20 ml of totally dissolved solution containing 2 mol of Mg and 1 mol of Al was prepared after which 1 g of biochar (produced from bovine bone) was added under continuous stirring while 3 M of NaOH was added drop-wisely until a pH of 10 was attained. The mixture was stirred for about 4 h and then centrifuged to separate the solid material from the liquid. The solid material was thoroughly washed with deionized water to remove the impurities before being oven-dried at 60 °C for 16 h. Also, in another study, biochar-montmorillonite composite was synthesized by firstly producing the biochar (feedstock: peanut shell) before being mixed with montmorillonite clay [13]. In this study, the biomass was pyrolyzed using a muffle furnace at 250 °C for 3 h in an oxygen-limited environment after which the produced biochar was allowed to cool and was grinded into powder form and passed through a 100-mesh screen. 30 g of the produced biochar was mixed with 30 g montmorillonite in 600 ml deionized water and thoroughly stirred with a magnetic stirrer for 2 h. The mixture was then centrifuged to separate the solid material from the liquid and then dried with an oven at 105 °C.

4 Types of Clay-Biochar Composites

Different clay-biochar composites have been synthesized by various research based on the purpose of synthesis, available materials, and some other factors as given in Table 1. Types of clay-biochar composite include bentonite–biochar composite [18, 20–22], montmorillonite and red earth–biochar composite [19, 23], MgAl-LDH/biochar composite [4], biochar-montmorillonite composites [13, 32, 34], iron-clay-biochar composite [28], attapulgite-clay-biochar composite [29, 30], silica/zeolite–biochar composite [35], biochar-chitosan/clay nanocomposite [36], and montmorillonite /kaolinite-biochar composites [31, 37].

5 Interactions of Clay and Biochar in Composite Materials

Biochar can be produced using different materials such as plant waste, food waste, sewage sludge, and agriculture crop residues which are abundant and easy to collect [39]. An environmentally favorable carbonaceous material with a large specific surface area is called biochar [40]. On the other hand, due to their unique physical and chemical characteristics and potential uses, clay minerals are receiving more attention in the field of materials science and analytical sciences as they are highly helpful for contaminants removal from the environment [41]. The colloidal component of sediment, soil, and rocks is made up primarily of clay minerals, which are hydrous aluminosilicates [42]. In addition, the clay minerals also have a significant impact on the environment because they act as natural adsorbents for pollutants by accepting ions during ion exchange and adsorption or both [43].

Due to the influence of abiotic and/or biotic processes on its characteristics and adsorption capacity and its low surface area, biochar appears to be less promising than activated carbon in the context of the adsorptive removal of pollutants from the environment [44]. Therefore, designing the composite from both biochar and clay can be more efficient in the removal of pollutants from the environment. The clay minerals interact with biochar along with combination of Si and Al that can act as binding agents. Additionally, an organo-mineral complex is created when the clay

Table 1 Types of clay-biochar composites

Types of clay-biochar composites	Clay	Biomass	Ratio of clay to biomass	Carbonization temperature (°C)	Carbonization time (min)	Ratio of clay to liquid	References
Bentonite–biochar composite	Bentonite	Cassava peel *Alternanthera philoxeroides* sweet sorghum bagasse *Prosopis Juliflora*	1:2 1:5 1:5 –	500 300 400 400–500	60 120 – –	25 g: 500 ml 2 g: 500 ml – –	Ismadji et al. [18] Jing et al. [21] Fosso-Kankeu et al. [20] Khandelwal et al. [22]
Montmorillonite and red earth–biochar composite	Montmorillonite and red earth	Cotton woods Municipal waste	1:5 1:5	500 500	30 30	50 g: 2000 ml 50 g: 2000 ml	Premarathna et al. [23] Borthakur et al. [19]
MgAl-LDH (Layered Double Hydroxide)/biochar composite	MgAl-LDH	Bovine bone	–	–	–	9.71 g: 20 ml	Meili et al. [4]
Biochar-montmorillonite composites	Montmorillonite	Peanut shell Cauliflower leaves Bamboo powder	– – 1:1	250 500 300, 350, 400, 450 and 500	120 360 60	30 g: 600 ml – –	Wang et al. [13] Liang et al. [32] Chen et al. [34]
Iron-clay-biochar composite	Kaolinite and bentonite	Bamboo	–	250, 350, 450 and 550	30	–	Rawal et al. [28]

(continued)

Table 1 (continued)

Types of clay-biochar composites	Clay	Biomass	Ratio of clay to biomass	Carbonization temperature (°C)	Carbonization time (min)	Ratio of clay to liquid	References
Attapulgite-clay-biochar composite	Attapulgite	Bagasse Potato stem *Macadamia* nutshells/ groundnut shells Cauliflower leaves	1:5 1:5 – 1:5	700 500 365, 555 and 700 500	240 360 30 360	4 g: 50 ml 2 g: 80 ml 30 g: 120 ml 4 g: 200 ml	Chen et al. [29] Li et al. [30] Qhubu et al. [38] Wang et al. [13]
Silica/zeolite–biochar composite	Silica or zeolite	Date palm waste	–	600	180	4 g: 1000 ml	Ahmad et al. [35]
Biochar-chitosan/clay nanocomposite	Montmorillonite clay	Residual bark chips	–	600	120	–	Arabyarmohammadi et al. [36]
Montmorillonite / kaolinite-biochar composites	Montmorillonite and kaolinite	Oak leaves Bamboo, bagasse and hickory chips	– 1:5	600 600	60 60	– 2 g: 500 ml	Gao and Goldfarb [37] Yao et al. [31]

that is attached to biochar's surface is injected into its interior pores [31]. Therefore, there are several mechanisms of interactions between clay minerals and biochar:

1. The surface interactions between clay minerals and biochar through direct electrostatic interaction, ligand exchange reactions, H-bonding, and cation bridging [45, 46].
2. The electron donor–acceptor (EDA) interactions between clay minerals and biochar can occur [45, 47].
3. Biochar releases soluble organic molecules that can be intercalated with clay minerals [45, 48].
4. Clay minerals' interlayer water is replaced by neutral organic molecules and is bounded by organic compounds, as occurs with smectites and binding of organic compounds as occur with kaolinite during H-bond and/or strong dipole interactions [48].
5. Also, the interactions can be hydrogen-π interactions between clay minerals by H silanol groups and by the face of electron-rich π-system of the aromatic ring in biochar, n-π electron donor–acceptor (EDA) interactions between a basal siloxane surface (clay minerals) and a nitro aromatic compound (biochar) [49].

6 Characterization of Clay-Biochar Composite

The X-ray diffraction (XRD), Fourier transform infrared spectroscopic (FTIR), scanning electron microscopy (SEM), EDX spectrum, and BET surface area are used to characterize the clay-biochar composites. There are some previous studies that described the differences between biochar and clay-biochar. The modification of biochar by clay has received wide attention from many researchers to remediate soil and water pollution. They proved that the modification of biochar with clay improves the surface area and enhances the functional group. Also, they mentioned that the clay distributes in the porous structure of biochar [20]. Table 2 presents the characteristics and properties of different clay-biochar composite.

6.1 X-Ray Diffraction (XRD) Analyses

The X-ray diffraction (XRD) is used to explore mineralogical composition of clay-biochar composite [54]. Yao et al. [31] described the modification of biochar by montmorillonite. The results of XRD analyses confirmed that the production of clay-biochar composites was successful where the clay (montmorillonite) was implanted onto the carbon surfaces of the biochar matrix. Also, they mentioned that the quartz (SiO_2) was found in clay-biochar composites and it was a common mineral within biochars. Another study for XRD analysis comparing between biochar and clay-biochar composite by Wang et al. [13] mentioned that the two diffraction peaks at $2\Theta = 11$ and 24.5° indicated biochar, while for montmorillonite-biochar showed

Table 2 Physical and chemical properties of different clay-biochar composites

Type of Clay-biochar composite	Mineral type and biomass	pH	BET Surface area (m^2 g^{-1})	Total pore volume (cm^3/g)	Elemental composition (%)											References
					N	C	H	S	O	Mg	Al	Si	K	Ca	Fe	
Montmorillonite-biochar composite	Montmorillonite and municipal solid waste	9.51	8.72	–	–	–	–	1.66		ND	8.66	46.4	ND	20.1	8.84	Premarathn et al. [23]
Bentonite-biochar composite	5% Bentonite and kelp	10.10	29.2	0.0195	1.54	26.2	0.42	0.0014	8.37	0.0012	0.0003	0.0024	0.0302	0.0021	0.0003	Sewu et al. [50]
Bentonite-biochar composite	10% Bentonite and kelp	10.10	2.30	0.0043	1.33	23.3	0.25	0.0014	5.40	0.0008	0.0004	0.0025	0.0248	0.0020	0.0006	Sewu et al. [50]
Bentonite-biochar composite	20% Bentonite and kelp	10.30	6.62	0.0211	0.68	20.2	0.21	0.0011	3.03	0.0006	0.0009	0.0083	0.0106	0.0018	0.0010	Sewu et al. [50]
Red earth-biochar composite	Red earth and municipal solid waste	8.99	8.44	–	–	–	–	ND		ND	12.8	44.3	7.9	12.3	19.5	Premarathn et al. [23]
Montmorillonite-biochar composite	Montmorillonite and municipal solid waste	–	7.703	0.0200	–	–	–	–	–	–	–	–	–	–	–	Borthakur et al. [19]
Natural red earth-biochar composite	Natural red earth and Municipal solid waste	–	18.711	0.0560	–	–	–	–	–	–	–	–	–	–	–	Borthakur et al. [19]
Montmorillonite-biochar composite	Montmorillonite and bamboo	–	408.1	–	0.25	83.3	2.26	–	12.4	0.14	0.68	–	0.33	0.21	0.23	Yao et al. [31]
Montmorillonite-biochar composite	Montmorillonite and bagasse	–	407.0	–	0.75	75.3	2.25	–	18.9	0.22	0.75	–	0.32	0.85	0.47	Yao et al. [31]
Montmorillonite-biochar composite	Montmorillonite and hickory chips	–	376.1	–	0.28	80.9	2.21	–	15.1	0.19	0.32	–	0.11	0.57	0.15	Yao et al. [31]

(continued)

Table 2 (continued)

Type of Clay-biochar composite	Mineral type and biomass	pH	BET Surface area (m^2 g^{-1})	Total pore volume (cm^3/g)	Elemental composition (%)											References
					N	C	H	S	O	Mg	Al	Si	K	Ca	Fe	
Kaolinite-biochar composite	Kaolinite and bamboo	–	239.8	–	0.25	81.0	2.15	–	15.9	0.05	0.30	–	0.07	0.19	0.08	Yao et al. [31]
Kaolinite-biochar composite	Kaolinite and bagasse	–	328.6	–	0.74	70.2	2.44	–	24.4	0.16	0.53	–	0.06	0.88	0.46	Yao et al. [31]
Kaolinite-biochar (hickory chips) composite	Kaolinite and hickory chips	–	224.4	–	0.33	78.1	2.11	–	18.1	0.18	0.51	–	0.05	0.52	0.04	Yao et al. [31]
Attapulgite-biochar composite	Attapulgite and cauliflower leaves	–	68.62	0.1010		67.9	–	0.03	22.4	1.75	0.58	1.55	–	5.3	0.41	Wang et al. [13]
Magnetic attapulgite-biochar composite	Attapulgite and cauliflower leaves		74.06	0.1270		51.4		0.05	25.2	1.32	0.25	0.87		2.9	17.3	Wang et al. [13]
Kaolinite-biochar composite	Kaolinite and pine cone	8.50	10.9	–	–	–	–	–	–	–	–	–	–	–	–	Olu-Owolabi et al. [51]
Kaolinite-biochar composite	Kaolinite and papaya seed	8.70	10.0	–	–	–	–	–	–	–	–	–	–	–	–	Olu-Owolabi et al. [51]
Montmorillonite-biochar composite	Montmorillonite and cauliflower leaves	–	37.4	0.0969	–	24.9	–	–	38.2	1.05	4.54	22.4	–	3.43	2.32	Liang et al. [32]

(continued)

Table 2 (continued)

Type of Clay-biochar composite	Mineral type and biomass	pH	BET Surface area (m^2 g^{-1})	Total pore volume (cm^3/g)	Elemental composition (%)											References
					N	C	H	S	O	Mg	Al	Si	K	Ca	Fe	
Magnetic montmorillonite-biochar composite	Montmorillonite and cauliflower leaves	–	67.8	0.1478	–	26.9	–	–	39.7	0.74	2.36	9.47	–	0.73	19.1	Liang et al. [32]
Montmorillonite-biochar composite	Montmorillonite and wheat straw	–	112.6	0.6040	1.85	58.8	1.16	–	27.0	–	–	–	–	–	–	Zhang et al. [52]
Montmorillonite-biochar composite	Montmorillonite and bamboo	–	156	0.1382	0.35	46.2	1.69	ND	–	–	–	–	–	–	–	Viglašová et al. [2]
Montmorillonite-biochar composite	Montmorillonite and municipal solid waste	9.46	6.51	–	–	–	–	–	–	–	–	–	–	–	–	Ashiq et al. [53]

four peaks at 2Θ = 5.7, 20.7, 34.9 and 60.8°. In addition, quartz (SiO_2) was a common impurity in clay with a sharp peak at 2Θ = 28.8°. Song et al. [55] reported that the main mineral component in the studied clay-biochar composite were silica and the secondary component was beidellite. Also, the XRD patterns showed the montmorillonite filled on biochar by four typical peaks at 6.5° ($d = 13.6$ Å), 17.2° ($d = 5.2$ Å), 19.9° ($d = 4.46$ Å) and 35.0° ($d = 2.6$ Å). In another study conducted in the modification of biochar by montmorillonite and kaolinite, the results revealed two peaks with centers at 2Θ = 24° and 43° corresponding to the strong and weak diffraction peaks respectively which indicated graphite (24°) and amorphous nature of carbon (43°) [56]. Additionally, the clay-biochar XRD pattern displayed primary reflection at 8.77, which is entirely lacking in both clay and biochar. The variations in the clay-biochar results demonstrated that the production technique employed successfully incorporated biochar onto the clay matrix [56].

6.2 Scanning Electron Microscopy (SEM)

Fosso-Kankeu et al. [20]mentioned that the image of biochar can be seen as rod-like structure and protrusions while the bentonite particles look like small lumps, and therefore, the surface texture for bentonite-biochar composite has a surface area larger than pristine biochar. In a research by Yao et al. [31], the SEM imaging of the clay-biochar composites showed that the surface area of the clay-biochar was covered by thin film structures which was also confirmed by the energy dispersive X-ray spectroscopy (EDX). In both the SEM imaging and the EDX spectrum, extremely high peaks for silicon, sodium, aluminum, calcium, iron, and magnesium could be seen on the clay-biochar composites surface, which are the main indicative of clay minerals' elemental composition [31]. Premarathna et al. [23] prepared montmorillonite-biochar and red earth-biochar, SEM images of the two composites showed that the pores present on the surfaces of biochar were able to remove tetracycline by enhancing surface adsorption. Also, the images of the composites from the SEM showed that clay particles bonded onto the surfaces of biochar that made the surfaces of the biochar to appear more rough and enhance the adsorption by the reactive surface than pristine biochar. However, the biochar pores remained open to the adsorbate molecules because the clay particles did not completely cover the biochar surfaces [23]. Likewise, modified biochar with montmorillonite with three temperatures (200, 350 and 700 °C) was applied for zinc removal [55]. It was observed that montmorillonite was bonded on the biochar appearing like scales. At 200 °C, the montmorillonite particles might block the pores of biochar. At 350 °C, the montmorillonite particles adhered to the biochar surfaces and at 700 °C, the biochar surfaces developed a lamellar structure. From the results, the high temperate changed the morphology of biochar loaded with montmorillonite. In addition, the SEM-EDS of the attapulgite-biochar composite showed that the high temperature led to resurgence of C and O atoms, whereas the Si, Al, and Mg concentration dwarfed [38]. Furthermore, both the Transmission Electron Microscope (TEM) and SEM images showed that pyrolyzing the mixture of biomass and iron-clay slurry resulted in the nanostructured minerals phases within the biochar's porous structure [28]. In a previous study conducted by Rallet et al. [56], it showed that clay has a smooth and hollow surfaces, while biochar has a porous structure with rough surface. Hence, the clay particles were precipitated on the biochar surface but not entirely cover the whole surface.

6.3 *Surface Area*

Surface area is an important property of clay-biochar composites that needs to be studied because it affects their performance. Yao et al. [31] modified biochar by kaolinite and montmorillonite, the raw material treated with kaolinite decreased surface area, probably due to kaolinite may cover/clog the pores on the biochar. Another research mentioned that the BET surface area of the clay-biochar composites was twofold times that of pristine biochar which may be as a result of the precipitation of clay particles on the surfaces of biochar [23]. Likewise, in another research, it was reported that the BET surface area of biochar was 2.79 m^2/g, while it was 6.18 m^2/g for montmorillonite-biochar [13]. Also, Song et al. [55] revealed that the montmorillonite-biochar composite exhibited larger surface area at higher pyrolysis temperature.

6.4 *Fourier-Transform Infrared Spectroscopic (FTIR)*

The FTIR spectra are used to investigate surface functional group of the clay-biochar composite. There are many studies to describe the differences of the FTIR spectra between clay-biochar composites and pristine biochar. One of these studies by Premarathna et al. [23] conveyed that the FTIR spectra of clay-biochar composites revealed significant differences compared to biochar due to the introduction of Si–O functional groups onto clay-biochar. Also, the FTIR analysis of attapulgite-biochar showed the presence of absorption peaks at 1139 and 1027 cm^{-1} which were referred to the biochar C–O and attapulgite [38]. Another research of the FTIR spectrum of montmorillonite-biochar by Wang et al. [13] revealed that the peaks at 3620, 519, and 468 cm^{-1} were assigned to −NH, Fe–O, and Si–O–Si, respectively. In this research, the FTIR demonstrated that the montmorillonite-biochar showed an oxygen functional group, which increased its adsorption ability. As well, the hydroxyl peak got weaker with increasing pyrolysis temperature [55]. The obtained FTIR spectrums of the clay-biochar composites have C=O, C=C, Si–O–Si, Al–OH–Al, and Si–O–Al at 1597, 1442, 1018, 875, 421 cm^{-1}, where virtually the same functional groups were detected in clay (3695, 3621, 1633, 991, 793, 911, 680, and 519 cm^{-1}) and biochar (1646, 1498, 1181, and 913 cm^{-1}) with low intensities [56].

6.5 CHNS Analyses and Energy Dispersive X-Ray Spectroscopy (EDX) Spectra

The CHNS analyses are used to describe the content of elements in clay-biochar composites. Hence, modification of biochar with clay minerals could change the metal contents of the engineered biochars. Yao et al. [31] mentioned that the content of oxygen in clay-biochar composite (using kaolinite and montmorillonite as clay) is more than that of biochar. Likewise, elemental analysis showed that both kaolinite and montmorillonite modification dramatically enhanced the biochar aluminum and iron content [31]. Also, in this study, montmorillonite amendment increased the biochar's sodium content. The EDX spectra of clay-biochar composites compared with other spectra provided evidence for the existence of clay on the biochar surface [56]. Furthermore, Wang et al. [13] showed that the EDS analysis revealed that the two main compositions of biochar were carbon and oxygen, while the typical elements of montmorillonite were silicon, oxygen, aluminum, magnesium, calcium, and iron. In addition, the EDS spectrum of the montmorillonite-biochar confirmed high peaks for silicon, oxygen, aluminum, magnesium, calcium, and iron. Similarly, the EDX spectra of clay presented high peaks of Si, Al, O, and Fe, which are the main metal composition [56]. Nevertheless, the chemical compositions in biochar were C, O, and Ca.

7 Optimization and Tuning of Clay-Biochar Composite for Target Application

The manufacture of sustainable biochar has drawn more attention in recent years due to its flexible physicochemical features and potential for use in a variety of industries. There have been extensive investigations done to characterize biochar generated from different feedstock and utilizing various production procedures and processing conditions. The major factors to be considered in determining the qualities of biochar required for particular applications are (i) choice of feedstocks and (ii) biochar production procedures [57]. Therefore, the choice of feedstock, tuning, and optimization of the production process are crucial for producing biochar with the required qualities. However, further clarification of these correlations is necessary for end users and stakeholders in biochar to be able to predict the physiochemical properties of biochar from specific feedstocks and production conditions, evaluate potential side effects of biochar use [58] and clay-biochar composites.

The negative consequences on human health make heavy metal poisoning of water bodies a topic that is currently receiving more attention. Despite the outstanding adsorption performance of biochar, it has undergone a number of modifications to increase its adsorption capacity, overcome the challenge of particle separation, and reduce the problems associated with secondary pollution.

To protect soil and water through intensive agricultural practices as well as significant industrial and transportation activities, a sustainable management of the environment and agriculture is essential. A promising tool to address these challenges could be the application of clay-biochar composites. Then, modification of biochar could be used in a variety of applications, including as sustainable agriculture and removing pollution [59]. Biochar modification enables the achievement of biochar properties which are optimum for particular applications through improving the beneficial biochar properties [59]. Clay minerals have a unique attraction for contaminants removal from contaminated sites [60, 61]. There are many types of clay minerals used to remove of contaminants from soil and water such as kaolinite, montmorillonite, bentonite and smectite. On the other hand, biochar has advanced properties such as high porosity, high functional groups, specific surface area, and cation exchange capacity [62]. Furthermore, modification of biochar with clay minerals can enhance the functionality of the composite to remove contaminants from the environment [31]. For instance, co-pyrolysis of montmorillonite and bamboo powder increased the maximum adsorption capacity of the composite for 34.72 mg P g^{-1} for PO_4^{3-} and this is due to the electrostatic attraction or ionic bonding between the PO_4^{3-} and cations present in the clay-biochar composite such as Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+} [34]. Because of improved surface complexation, attapulgite-biochar composites have been successful at immobilizing As and Cd in river sediments [13]. One of the factors to be considered in preparing clay-biochar composite is the pyrolysis temperature. There are many studies that showed a successful production clay-biochar composite at 600 °C for 1 h [63, 64, 65].

8 Future Research Challenges and Prospects

After entering the twenty-first century, biochar has become a focus of multidisciplinary research. Due to its unique qualities, widespread applications, and bright future, in light of issues with food security, environmental pollution, and energy scarcity, basic and practical research on the use of biochar in agriculture, the environment, and energy has significantly risen. Even if there are various disagreements regarding biochar research, numerous studies have shown its significance from the standpoints of scientific development and practical application.

By 2050, it is anticipated that the world's demand for food will have doubled because of an expanding and more demanding population. Additionally, the production of food is in competition with the increased need for biofuels. Environmental costs associated with the earlier agricultural boom included water eutrophication, the extinction of species and crop varieties, and a decline in ecosystem services. Using the "green revolution instruments," it is unclear whether agriculture will be able to grow as it did in the previous 50 years. We require strategies to enhance nutrient cycling and usage effectiveness, as well as to restore and sustain soil fertility. There are several grounds to believe that future environmental harm and resource depletion will reduce agricultural productivity. One of the biggest problems confronting humanity may be increasing agricultural productivity while conserving resources and reducing the impact on the environment. A more environmentally friendly revolution is required [66].

The study of biochar systems is a highly interdisciplinary field that draws on soil, forestry, and agricultural sciences as well as technologies for producing renewable energy. In order to handle the problems caused by the conflicts and synergies between growing crops for multiple objectives, such as energy production, carbon sequestration, or food, biochar offers special solutions. Biomass is burnt under a low oxygen supply to make biochar, which is carbonized organic matter. By lengthening the half-life of biomass, which would otherwise decay or be burnt, carbonization would slow down the carbon cycle. Such pyrogenic carbon has been demonstrated through research and historical data to play essential roles in soil fertility. Additionally, a sizable carbon sink would be produced by the resistance of carbonized organic materials and its non-fuel use (biochar) as a soil amendment. Despite the fact that biochar has ancient origins and can be found in naturally occurring (Chernozems or Mollisols) or artificially (Terra Preta in the Amazon) modified soils, integrating it into contemporary land-use systems is difficult and requires scientifically sound foundations as well as the ability to pass environmental and life cycle assessments [67].

Recent studies have shown that biochar may be used to remove contaminants from polluted water and soil ecosystems as well as amend soil for agricultural cultivation. Critical debate on the benefits and drawbacks of biochar for diverse soil applications (such as soil amendment and/or decontamination) is required to encourage the commercialization of biochar for large-scale uses [68] and also its composite with clay.

A significant number of aromatic recalcitrant organic pollutants are produced by various paper, oil, leather, and textile industries and released into the environment, posing serious health risks to all living things. The leakage of residual dyes from the textile industry into water bodies upsets the ecosystem because they accumulate in aquatic life and kill it. This contaminated water is frequently utilized in agriculture and eventually gets to people via bioaccumulation processes. The synthetic dyes that are widely employed in the textile industry can cause cancer and genetic mutation in people when they come into touch with them physically or through the food chain. Before being released into nature, the harmful color effluent from the textile industries could be controlled through physical, chemical, and biological methods including oxidation, phytoremediation, membrane filtration, chemical, and adsorbents like biochar or microbes [66].

Environmental pollution has become a big issue on a global scale in recent years, negatively affecting both human health and the economy. Because soil's environmental characteristics are so intricate, repair and treatment are more difficult and expensive. Sustainable materials such as biochar, biomaterials, and composites offer an economical and effective remediation approach in this regard. Exactly, the inclusion of metal oxides, surface agents, and nanomaterials can give biochar and its related composites unique features.

Significant attention is given to soil remediation, particularly the removal of heavy metals using composites based on biochar [69]. Therefore, it is imperative to conduct more study on the synthesis of more eco-friendly materials such as clay-biochar composite in the heavy metal remediation, contaminants immobilization and for other environmental use.

9 Conclusion

In this chapter, clay-biochar composites are well discussed with their different application as gathered from previous studies. In this chapter, it could be deduced that smaller particle size, higher stability, lamellar structure, high surface area, numerous surface hydroxyl and silanol groups, and high ion exchange capacity are among the prominent characteristics of clays which make them excellent candidates for environmental and agricultural applications. These unique features give clay good adsorption potentials. However, the combination of clay with biochar improved this features, hence, enhanced its adsorbent properties. Clay-biochar composites have been synthesized in numerous studies and were found to be more effective in the removal of contaminants such as methylene blue, cadmium, ammonium, cadmium, arsenic, and nitrate. Moreover, it is eco-friendly, more effective, and easy to produce.

References

1. Djomgoue, P., Njopwouo, D.: FT-IR spectroscopy applied for surface clays characterization. J. Surf. Eng. Mater. Adv. Technol. **3**(04), 275 (2013)
2. Viglašová, E., Galamboš, M., Danková, Z., Krivosudský, L., Lengauer, C.L., Hood-Nowotny, R., Soja, G., Rompel, A., Matík, M., Briančin, J.: Production, characterization and adsorption studies of bamboo-based biochar/montmorillonite composite for nitrate removal. Waste Manag. **79**, 385–394 (2018)
3. Franciski, M.A., Peres, E.C., Godinho, M., Perondi, D., Foletto, E.L., Collazzo, G.C., Dotto, G.L.: Development of CO_2 activated biochar from solid wastes of a beer industry and its application for methylene blue adsorption. Waste Manag. **78**, 630–638 (2018)
4. Meili, L., Lins, P.V., Zanta, C.L.P.S., Soletti, J.I., Ribeiro, L.M.O., Dornelas, C.B., Silva, T.L., Vieira, M.G.A.: MgAl-LDH/Biochar composites for methylene blue removal by adsorption. Appl. Clay Sci. **168**, 11–20 (2019)
5. Rajapaksha, A.U., Chen, S.S., Tsang, D.C., Zhang, M., Vithanage, M., Mandal, S., Gao, B., Bolan, N.S., Ok, Y.S.: Engineered/designer biochar for contaminant removal/immobilization from soil and water: potential and implication of biochar modification. Chemosphere **148**, 276–291 (2016)
6. Kwiatkowski, M., Kalderis, D.: A complementary analysis of the porous structure of biochars obtained from biomass. Carbon Lett. **30**(3), 325–329 (2020)
7. Leng, L., Xiong, Q., Yang, L., Li, H., Zhou, Y., Zhang, W., Jiang, S., Li, H., Huang, H.: An overview on engineering the surface area and porosity of biochar. Sci. Total Environ. **763**, 144204 (2021)
8. Ok, Y.S., Bhatnagar, A., Hou, D., Bhaskar, T. and Mašek, O.: Advances in algal biochar: production, characterization and applications. Bioresour. Technol. **317**, 123982 (2020)
9. Dai, Y., Zheng, H., Jiang, Z., Xing, B.: Combined effects of biochar properties and soil conditions on plant growth: a meta-analysis. Sci. Total Environ. **713**, 136635 (2020)

10. Li, F., Cao, X., Zhao, L., Wang, J., Ding, Z.: Effects of mineral additives on biochar formation: carbon retention, stability, and properties. Environ. Sci. Technol. **48**(19), 11211–11217 (2014)
11. Arif, M., Ali, S., Ilyas, M., Riaz, M., Akhtar, K., Ali, K., Adnan, M., Fahad, S., Khan, I., Shah, S., Wang, H.: Enhancing phosphorus availability, soil organic carbon, maize productivity and farm profitability through biochar and organic–inorganic fertilizers in an irrigated maize agroecosystem under semi-arid climate. Soil Use Manag **37**(1), 104–119 (2021)
12. Palansooriya, K.N., Shaheen, S.M., Chen, S.S., Tsang, D.C., Hashimoto, Y., Hou, D., Bolan, N.S., Rinklebe, J., Ok, Y.S.: Soil amendments for immobilization of potentially toxic elements in contaminated soils: a critical review. Environ. Int. **134**, 105046 (2020)
13. Wang, H., Tan, L., Hu, B., Qiu, M., Liang, L., Bao, L., Zhu, Y., Chen, G., Huang, C.: Removal of Cr (VI) from acid mine drainage with clay-biochar composite. Environment **28**, 32 (2019)
14. Shaheen, S.M., Niazi, N.K., Hassan, N.E., Bibi, I., Wang, H., Tsang, D.C., Ok, Y.S., Bolan, N., Rinklebe, J.: Wood-based biochar for the removal of potentially toxic elements in water and wastewater: a critical review. Int. Mater. Rev. **64**(4), 216–247 (2019)
15. Xiang, W., Zhang, X., Chen, J., Zou, W., He, F., Hu, X., Tsang, D.C., Ok, Y.S., Gao, B.: Biochar technology in wastewater treatment: a critical review. Chemosphere **252**, 126539 (2020)
16. Shi, Q., Wang, Y., Zhang, X., Shen, B., Wang, F., Zhang, Y.: Hierarchically porous biochar synthesized with CaCO3 template for efficient Hg0 adsorption from flue gas. Fuel Process. Technol. **199**, 106247 (2020)
17. Panwar, N.L., Pawar, A.: Influence of activation conditions on the physicochemical properties of activated biochar: a review. In: Biomass conversion biorefinery, pp. 1–23
18. Ismadji, S., Tong, D.S., Soetaredjo, F.E., Ayucitra, A., Yu, W.H., Zhou, C.H.: Bentonite-hydrochar composite for removal of ammonium from Koi fish tank. Appl. Clay Sci. **114**, 467–475 (2015)
19. Borthakur, P., Aryafard, M., Zara, Z., David, Ř, Minofar, B., Das, M.R., Vithanage, M.: Computational and experimental assessment of pH and specific ions on the solute solvent interactions of clay-biochar composites towards tetracycline adsorption: implications on wastewater treatment. J. Environ. Manag. **283**, 111989 (2021)
20. Fosso-Kankeu, E., Waanders, F.B., Steyn, F.W.: The preparation and characterization of clay-biochar composites for the removal of metal pollutants. In: 7th International Conference on latest Trends in Engineering and Technology (ICLTET'2015), pp. 54–57 (2015)
21. Jing, Y., Cao, Y., Yang, Q., Wang, X.: Removal of Cd (II) from aqueous solution by clay-biochar composite prepared from Alternanthera philoxeroides and bentonite. BioResources **15**(1), 598–615 (2020)
22. Khandelwal, N., Tiwari, E., Singh, N., Darbha, G.K.: Heterogeneously Porous Multiadsorbent Clay-Biochar surface to support redox-sensitive nanoparticles: applications of Novel Clay–Biochar–Nanoscale Zerovalent Iron Nanotrident (C-BC-nZVI) in continuous water filtration. ACS ES&T Water **1**(3), 641–652 (2021)
23. Premarathna, K.S.D., Rajapaksha, A.U., Adassoriya, N., Sarkar, B., Sirimuthu, N.M., Cooray, A., Ok, Y.S., Vithanage, M.: Clay-biochar composites for sorptive removal of tetracycline antibiotic in aqueous media. J. Environ. Manag. **238**, 315–322 (2019)
24. Wang, L., Rinklebe, J., Tack, F.M., Hou, D.: A review of green remediation strategies for heavy metal contaminated soil. Soil Use Manag. **37**(4), 936–963 (2021)
25. Roberts, K.G., Gloy, B.A., Joseph, S., Scott, N.R., Lehmann, J.: Life cycle assessment of biochar systems: estimating the energetic, economic, and climate change potential. Environ. Sci. Technol. **44**(2), 827–833 (2010)
26. Bilgiç, C.: Investigation of the factors affecting organic cation adsorption on some silicate minerals. J. Colloid Interface Sci. **281**(1), 33–38 (2005)
27. Gürses, A., Doğar, Ç., Yalçın, M., Açıkyıldız, M., Bayrak, R., Karaca, S.: The adsorption kinetics of the cationic dye, methylene blue, onto clay. J. Hazard. Mater. **131**(1–3), 217–228 (2006)
28. Rawal, A., Joseph, S.D., Hook, J.M., Chia, C.H., Munroe, P.R., Donne, S., Lin, Y., Phelan, D., Mitchell, D.R., Pace, B., Horvat, J.: Mineral–biochar composites: molecular structure and porosity. Environ. Sci. Technol. **50**(14), 7706–7714 (2016)

29. Chen, S., Zhou, M., Wang, H.F., Wang, T., Wang, X.S., Hou, H.B., Song, B.Y.: Adsorption of reactive brilliant red X-3B in aqueous solutions on clay–biochar composites from bagasse and natural attapulgite. Water **10**(6), 703 (2018)
30. Li, Y., Wang, Z., Xie, X., Zhu, J., Li, R., Qin, T.: Removal of Norfloxacin from aqueous solution by clay-biochar composite prepared from potato stem and natural attapulgite. Colloids Surf., A **514**, 126–136 (2017)
31. Yao, Y., Gao, B., Fang, J., Zhang, M., Chen, H., Zhou, Y., Creamer, A.E., Sun, Y., Yang, L.: Characterization and environmental applications of clay–biochar composites. Chem. Eng. J. **242**, 136–143 (2014)
32. Liang, G., Wang, Z., Yang, X., Qin, T., Xie, X., Zhao, J., Li, S.: Efficient removal of oxytetracycline from aqueous solution using magnetic montmorillonite-biochar composite prepared by one step pyrolysis. Sci. Total Environ. **695**, 133800 (2019)
33. Zhang, M., Gao, B., Yao, Y., Inyang, M.: Phosphate removal ability of biochar/MgAl-LDH ultra-fine composites prepared by liquid-phase deposition. Chemosphere **92**, 1042–1047 (2013)
34. Chen, L., Chen, X.L., Zhou, C.H., Yang, H.M., Ji, S.F., Tong, D.S., Zhong, Z.K., Yu, W.H., Chu, M.Q.: Environmental-friendly montmorillonite-biochar composites: facile production and tunable adsorption-release of ammonium and phosphate. J. Clean. Prod. **156**, 648–659 (2017)
35. Ahmad, M., Ahmad, M., Usman, A.R., Al-Faraj, A.S., Abduljabbar, A., Ok, Y.S., Al-Wabel, M.I.: Date palm waste-derived biochar composites with silica and zeolite: synthesis, characterization and implication for carbon stability and recalcitrant potential. Environ. Geochem. Health **41**(4), 1687–1704 (2019)
36. Arabyarmohammadi, H., Darban, A.K., Abdollahy, M., Yong, R., Ayati, B., Zirakjou, A., van der Zee, S.E.: Utilization of a novel chitosan/clay/biochar nanobiocomposite for immobilization of heavy metals in acid soil environment. J. Polym. Environ. **26**(5), 2107–2119 (2018)
37. Gao, L., Goldfarb, J.L.: Characterization and adsorption applications of composite biochars of clay minerals and biomass. Environ. Sci. Pollut. Res. **28**(32), 44277–44287 (2021)
38. Qhubu, M.C., Mgidlana, L.G., Madikizela, L.M., Pakade, V.E.: Preparation, characterization and application of activated clay biochar composite for removal of Cr (VI) in water: Isotherms, kinetics and thermodynamics. Mater. Chem. Phys. **260**, 124165 (2021)
39. Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S. and Ok, Y.S.: Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere **99**, 19–33 (2014)
40. Lehmann, J., Joseph, S.: Biochar for environmental management. In: Science and Technology. Earthscan, UK (2009)
41. Srinivasan, R.: Advances in application of natural clay and its composites in removal of biological, organic, and inorganic contaminants from drinking water. Adv. Mater. Sci. Eng. (2011)
42. Pinnavaia, T.J.: Intercalated clay catalysts. Science **220**(4595), 365–371 (1983)
43. Cadena, F., Rizvi, R., Peters, R.W.: Feasibility studies for the removal of heavy metals from solution using tailored bentonite. In: Hazardous and Industrial Wastes-Proceedings of the Mid-Atlantic Industrial Waste Conference, pp. 77–94 (1990)
44. Anderson, N., Jones, J.G., Page-Dumroese, D., McCollum, D., Baker, S., Loeffler, D., Chung, W.: A comparison of producer gas, biochar, and activated carbon from two distributed scale thermochemical conversion systems used to process forest biomass. Energies **6**(1), 164–183 (2013)
45. Joseph, S.D., Camps-Arbestain, M., Lin, Y., Munroe, P., Chia, C.H., Hook, J., Van Zwieten, L., Kimber, S., Cowie, A., Singh, B.P., Lehmann, J.: An investigation into the reactions of biochar in soil. Soil Res. **48**(7), 501–515 (2010)
46. Dultz, S.: Buchbesprechung: Organo-clay complexes and interactions. From S. Yariv and H. Cross (2002)
47. Keiluweit, M., Kleber, M.: Molecular-level interactions in soils and sediments: the role of aromatic π-systems. Environ. Sci. Technol. **43**(10), 3421–3429 (2009)
48. Matusik, J., Gaweł, A., Bielańska, E., Osuch, W., Bahranowski, K.: The effect of structural order on nanotubes derived from kaolin-group minerals. Clays Clay Miner. **57**(4), 452–464 (2009)

49. Trigo, C., Spokas, K.A., Cox, L., Koskinen, W.C.: Influence of soil biochar aging on sorption of the herbicides MCPA, nicosulfuron, terbuthylazine, indaziflam, and fluoroethyldiaminotriazine. J. Agric. Food Chem. **62**(45), 10855–10860 (2014)
50. Sewu, D.D., Lee, D.S., Tran, H.N., Woo, S.H.: Effect of bentonite-mineral co-pyrolysis with macroalgae on physicochemical property and dye uptake capacity of bentonite/biochar composite. J. Taiwan Inst. Chem. Eng. **104**, 106–113 (2019)
51. Olu-Owolabi, B.I., Diagboya, P.N., Mtunzi, F.M., Düring, R.A.: Utilizing eco-friendly kaolinite-biochar composite adsorbent for removal of ivermectin in aqueous media. J. Environ. Manag. **279**, 111619 (2021)
52. Zhang, J., Lu, M., Wan, J., Sun, Y., Lan, H., Deng, X.: Effects of pH, dissolved humic acid and Cu2+ on the adsorption of norfloxacin on montmorillonite-biochar composite derived from wheat straw. Biochem. Eng. J. **130**, 104–112 (2018)
53. Ashiq, A., Sarkar, B., Adassooriya, N., Walpita, J., Rajapaksha, A.U., Ok, Y.S., Vithanage, M.:Sorption process of municipal solid waste biochar-montmorillonite composite for ciprofloxacin removal in aqueous media. Chemosphere **236**, 124384 (2019)
54. Zhou, L., Chi, T., Zhou, Y., Lv, J., Chen, H., Sun, S., Zhu, X., Wu, H., Hu, X.: Efficient removal of hexavalent chromium through adsorption-reduction-adsorption pathway by iron-clay biochar composite prepared from *Populus nigra*. Sep. Purif. Technol. **285**, 120386 (2022)
55. Song, J., Zhang, S., Li, G., Du, Q., Yang, F.: Preparation of montmorillonite modified biochar with various temperatures and their mechanism for Zn ion removal. J. Hazard. Mater. **391**, 121692 (2020)
56. Rallet, D., Paltahe, A., Tsamo, C., Loura, B.: Synthesis of clay-biochar composite for glyphosate removal from aqueous solution. Heliyon **8**(3), e09112 (2022)
57. Xie, Y., Wang, L., Li, H., Westholm, L.J., Carvalho, L., Thorin, E., Yu, Z., Yu, X., Skreiberg, Ø.: A critical review on production, modification and utilization of biochar. J. Anal. Appl. Pyrol. **161**, 105405 (2022)
58. Chin, J.F., Heng, Z.W., Teoh, H.C., Chong, W.C., Pang, Y.L.: Recent development of magnetic biochar crosslinked chitosan on heavy metal removal from wastewater-Modification, application and mechanism. Chemosphere 133035 (2021)
59. Panahi, H.K.S., Dehhaghi, M., Ok, Y.S., Nizami, A.S., Khoshnevisan, B., Mussatto, S.I., Aghbashlo, M., Tabatabaei, M., Lam, S.S.: A comprehensive review of engineered biochar: production, characteristics, and environmental applications. J. Clean. Prod. **270**, 122462 (2020)
60. An, X., Wu, Z., Yu, J., Ge, L., Li, T., Liu, X., Yu, B.: High-efficiency reclaiming phosphate from an aqueous solution by bentonite modified biochars: a slow release fertilizer with a precise rate regulation. ACS Sustain Chem Eng **8**(15), 6090–6099 (2020)
61. Lazaratou, C.V., Vayenas, D.V., Papoulis, D.: The role of clays, clay minerals and clay-based materials for nitrate removal from water systems: a review. Appl. Clay Sci. **185**, 105377 (2020)
62. Qiu, B., Tao, X., Wang, H., Li, W., Ding, X., Chu, H.: Biochar as a low-cost adsorbent for aqueous heavy metal removal: a review. J. Anal. Appl. Pyrol. **155**, 105081 (2021)
63. Inyang, M., Gao, B., Zimmerman, A., Zhang, M., Chen, H.: Synthesis, characterization, and dye sorption ability of carbon nanotube–biochar nanocomposites. Chem. Eng. J. **236**, 39–46 (2014)
64. Zhang, M., Gao, B.: Removal of arsenic, methylene blue, and phosphate by biochar/AlOOH nanocomposite. Chem. Eng. J. **226**, 286–292 (2013)
65. Zhang, M., Gao, B., Yao, Y., Xue, Y., Inyang, M.: Synthesis of porous MgO-biochar nanocomposites for removal of phosphate and nitrate from aqueous solutions. Chem. Eng. J. **210**, 26–32 (2012)
66. Tilman, D., Cassman, K.G., Matson, P.A., Naylor, R., Polasky, S.: Agricultural sustainability and intensive production practices. Nature **418**(6898), 671–677 (2002)
67. Gupta, R., Pandit, C., Pandit, S., Gupta, P.K., Lahiri, D., Agarwal, D., Pandey, S.: Potential and future prospects of biochar-based materials and their applications in removal of organic contaminants from industrial wastewater. J. Mater. Cycl. Waste Manag. 1–25 (2022)

68. Mandal, S., Pu, S., Adhikari, S., Ma, H., Kim, D.H., Bai, Y., Hou, D.: Progress and future prospects in biochar composites: application and reflection in the soil environment. Crit. Rev. Environ. Sci. Technol. **51**(3), 219–271 (2021)
69. Lehmann, J.: Bio-energy in the black. Front. Ecol. Environ. **5**(7), 381–387 (2007)

Application of Clay-Biochar Composites as Adsorbents for Water Treatment

Luiz Daniel da Silva Neto, Ícaro Mychel Gomes Leite de Sá, Rafaela Gabriel, Pollyanna Vanessa dos Santos Lins, José Teixeira Freire, and Lucas Meili

Abstract Recently, biochar has been recommended as a supporting material for nanometric particles to prevent agglomeration and improve surface area. Among the conceivable uses, clay dispersion over biochar appears to be an intriguing and creative choice that allows for the simultaneous and synergistic exploitation of the adsorption capabilities of both materials. In fact, modifying biochar with clays to generate composites is projected to considerably increase its adsorptive activity, representing an important opportunity to broaden the uses of a sustainable low-cost adsorbent. In light of this, the purpose of this chapter is to investigate the adsorption of various contaminants on clays supported on biochar. The chapter will be divided into sections that cover the principles of clays, biochar, and their unique features, the main techniques of composite synthesis, and the use of these materials as adsorbents for various contaminants.

Keywords Biochar · Clay-like adsorbents · Carbonaceous material · Pollutants removal · Water treatment

1 Introduction

Clay minerals, which are plentiful in nature and are highly reactive geomaterials, have been employed for a variety of uses. Because of their low cost, availability, cation exchange capacity, strong removal efficiency, and selectivity, clay minerals have garnered a lot of interest as adsorbents for pollutants removal from aqueous media. However, because to their small surface area, weak affinity for organic contaminants, and difficulty in post-use recovery, this interest has been slow [1–3]. Clay adsorbents,

---

L. D. da Silva Neto · J. T. Freire
Drying Center of Pastes, Department of Chemical Engineering, Federal University of São Carlos (UFSCar), Suspensions, and Seeds, São Carlos, São Paulo 13565-905, Brazil

Í. M. G. L. de Sá · R. Gabriel · P. V. dos Santos Lins · L. Meili (✉)
Laboratory of Processes, Center of Technology, Federal University of Alagoas (UFAL), Maceió, Alagoas 57072-900, Brazil
e-mail: lucas.meili@ctec.ufal.br

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_6

are also often more effective when supported or disseminated over large surface area and low-cost porous substrates. Biochar is an intriguing alternative among these supporting materials because it combines strong textural features with a general environmental potential in terms of sustainability, low-cost manufacturing, and non-toxicity [4].

Biochar, also known as pyrochar, is a carbon-rich substance made from waste and biomass resources including wood, leaves, dung, and tree roots [5]. Because of its intrinsic features, such as oxygenated functional groups, large surface area, increased mineral content, and high cation exchange capacity, and biochar is a promising adsorbent in wastewater treatment [6]. Biochar has recently been recommended as a supporting material for nanometric particles in order to prevent agglomeration and improve surface area [7–11]. The dispersion of clays onto biochar is an fascinating and new approach that enables for the simultaneous and synergistic exploitation of both materials' adsorption characteristics. In fact, this modification to generate composites is projected to considerably increase the adsorptive capacity, and represents an important opportunity to broaden the uses of a sustainable low-cost adsorbent such as biochar in water treatment [4, 12].

Therefore, this chapter focus on the following subjects: (1) the main sources and the selection of biomasses; (2) the biochar production and main physic-chemical characteristics; (3) fundamentals about clays and modifications; (4) the synthesis and characteristics of clays-biochar composites; (5) clays-biochar composites application as adsorbents; and, finally, (6) the perspective and future directions of environmental uses of the clays-biochar composites.

2 Biomass Selection

Biomass sources cover a range of materials that can be used as raw materials to produce biochar. In general, the properties of biochar (BC) derive from the type of material (biomass) and the operational conditions of the conversion process (pyrolysis) used in the production of this coal. The definition of these factors directly interferes with the quality of the biochar produced and should be aligned with the application and destination of these products [4, 13].

The fulfillment of these requirements promotes a true diversification of materials, leading to a branch of new products with optimized characteristics. Thus, from the perspective of optimizing the production of biochar from the point of view of the type of material, a rigid selection of raw material is necessary, focusing on the physical–chemical characteristics of the final product to be produced and its employability. This methodology generates a critical view about the selection of the starting material [13].

Biomass sources are differentiated into groups according to their characteristics or origins. The most usual classification categorizes raw materials as biomass of non-woody vegetables, woody vegetables, and organic waste (agricultural, industrial, and urban) as shown in Table 1.

Table 1 Classification of raw material

Biomass origin		Biomass
Non-woody vegetables		Water hyacinth biomass [14];
Woody vegetables		Growing wood macaranga gigantea [15];
Organic waste:	(1) Agricultural	Torrefied rice [16], coconut inflorescence wastes [17], corn cob [18];
	(2) Urban	Municipal solid waste [19], sewage sludge [20];
	(3) Industrial	Waste rubber [21], plastic waste [22], paper mill sludge, and textile dyeing sludge [23]

Other forms of biomass classification are also considered. Dermirbas [24] classifies biomass according to origin, such as: vegetable, animal, and urban [24]. On the other hand, Cortez et al. [25] classify biomass according to the technological routes or levels of technological development adopted for its use, such as: traditional, modern, and improved [25]. Notably, several ways of biomass classifying can be considered, and this differentiation is fundamental to ensure that its use is carried out efficiently, to measure its impacts and potentials.

In general, the properties of each biomass (chemical composition, ash content and composition, nutrient content, moisture content, particle size and shape, density, among others) play a decisive role in the evaluation of its predisposition for use as biochar. Therefore, to understand the benefits and direct the applications of biochar, it is important to evaluate the physicochemical variations of the biomass [4].

The chemical components of plants (cellulose, hemicellulose, and lignin) and their derivatives undergo different reactions during pyrolysis, such as: dehydration hemicellulose degradation, cellulose degradation, and degradation of lignin, with release of gases. The combination of these processes is complex, however it can be observed that lignin (the last component to be degraded) strongly influences the final structure of biochars, such as micro and macroporosity. This relationship between lignin and structural properties is even more evident when the pyrolysis conditions were milder [4, 26].

Considering the chemical composition of the biomass, Maia et al. makes an interesting differentiation of biochar based on their composition and consecutive physical properties [26]. According to the author, biomass with different lignin contents produces biochar with notable anatomical differences (such as porosity, grain size). Thus, the interrelation of the chemical and physical properties of the material produced is clear.

Thus, one can think of organofunctionalized raw materials that are used to produce a biochar with a specific purpose. For example, biochar with high content of nutrient and mineral, such as agricultural residues, are often used as soil amendments to improve fertility, while those with high recalcitrance can function in carbon fixation [13].

In addition, other external factors contribute to the differentiation of the biochar produced. Moisture, for example, is a factor of great influence on transport, storage, and production process costs. Biomass with high moisture content (above 30%) impacts the total time of the pyrolysis process, as they can: increase the heating rate [27] cause inconstant maximum temperatures [28] and hampers the thermal transfer of heat in the biomass, due to the convective transport of water vapors [29].

Thus, it is understood that it is possible to produce biochar from any source of biomass. The limitation, however, is related to the differences in the chemical composition and morphology of these materials, as well as in the storage, transport and conversion that will produce materials with different characteristics, such as nutrient content, specific area, porosity, pH, ion exchange capacity, recalcitrance among others.

3 Biochar

Different methodologies are used to convert biomass into products with higher added value. This biomass can come from residues from various segments, such as agriculture, agricultural crops, woody vegetables, urban, and industrial effluents. Biomass-derived products are used in the generation of energy in the form of heat and electricity, or in the production of biofuels, such as ethanol, biodiesel, biogas, bio-oil, and biochar [30].

Pyrolysis is a process of thermal decomposition of biomass, in the absence or in limited oxygen conditions. As products, a gas phase (H_2, CO_2, CH_4, etc.), a liquid phase (bio-oil, tar), and a solid phase (biochar) are obtained. Biochar is the solid fraction obtained from the pyrolysis process, consisting mostly of carbon sp^2 domains randomly arranged, with empty spaces between them. Among the properties of biochar, the mechanical stability, high surface area, porous structure, and the presence of different functional groups on the surface stand out [31]. These characteristics are influenced by the composition and size of biomass particles. In addition to the type of biomass chosen, pyrolysis parameters also influence the gas/liquid/solid ratio produced, parameters such as temperature, reaction time, and heating rate [21–23]. Table 2 shows some of the main types of pyrolysis, and the characteristic conditions of each type of.

Table 2 Types of pyrolysis [38]

Pyrolysis	T (°C)	Time (s)	Heating rate (°C.s^{-1})	Biochar (%)	Bio-oil (%)	Gas (%)
Slow	350–700	300–126,000	0.02–0.83	30–35	18–20	30–35
Intermediate	400–650	60–900	1.67–5.00	15–25	40–60	20–30
Flash	500–900	< 1	> 1000	15–25	60–80	10–20
Speedy	450–1400	0.2–10	1000–10,000	12–25	70–75	13–30
Vacuum	300–600	0.001–1	6–60	25–30	45–50	15–20

The different proportions of biomass constituents favor the formation of some products. In general, cellulose and hemicellulose favor the formation of bio-oil and gas; lignin assists in the formation of gases and biochar; proteins and lipids in microalgae tend to form higher proportions of bio-oil and gas [32, 35, 36].

Temperature Effect

The temperature of the pyrolytic process plays an important function in the composition of the products. Hemicellulose thermally decomposes at 200–300 °C, cellulose is decomposed in the region of 300–380 °C, and the thermal decomposition range of lignin is 200–300 °C. Thus, the increase in the temperature of the pyrolysis process favors the formation of bio-oil and gas fractions [32, 37].

In different studies, Santos et al. [39, 40] evaluated the influence of the temperature of the pyrolysis process on the percentages of biochar, bio-oil and gas fractions, using *Wodyetia bifurcata* and *Syagrus oleracea* as a biomass source, according to Table 3 [39, 40].

Thus, it was observed that the increase in process temperature favors the formation of liquid and gaseous fractions and decreases the percentage of biochar production.

Heating rate

In pyrolysis, the rate of heating influences the proportion of products, for example, the formation of biochar is favored in slow pyrolysis. In addition, flash and rapid pyrolysis are most used when the goal is bio-oil production. Thus, the increase in the rate of heating tends to the formation of bio-oil [41, 42].

In their studies, Klinger et al. [41] the effect of the heating rate on the pyrolysis process of *Brassica napus*. Thus, a decrease in biochar production was observed with the increase in the heating rate. The same effect was observed in the work of Aysu and Küçük [43], where *Ferula orientalis* was used as biomass in pyrolysis. Similarly, the decrease in the biochar fraction, and consequently, an increase in the amounts of bio-oil and gas were favored with the increase in the rate of heating.

Effect of residence time

The residence time is the contact time of the biomass inside the reactor during pyrolysis. This variable has a negative correlation with biochar yield, other studies also observe this effect [44–46]. This negative trend is expected, since it is possible to further volatilization of mass in longer conditions of pyrolysis. In pyrolysis, shorter residence times (seconds or minutes) are recommended when the goal is to obtain

Table 3 Pyrolysis of *Wodyetia bifurcata* and *Syagrus oleracea*. [39, 40]

Yield (%)	*Wodyetia bifurcate*				*Syagrus oleracea*			
	400 °C	500 °C	600 °C	700 °C	400 °C	500 °C	600 °C	700 °C
Biochar	42,9	38,6	29,6	20,3	34,4	28,6	24,2	21,1
Bio-oil	36,5	38,2	42,8	49,5	42,4	46,1	48,0	49,3
Gas	20,6	23,2	27,6	30,2	23,2	25,3	27,8	29,6

bio-oil [47]. However, short times can compromise the heat transfer on the surface of the particles, thus impairing the complete conversion of biomass in the pyrolysis process.

Biochar Activated

In adsorption processes using biochar as adsorbent, the properties of greatest interest are the functional groups present, the surface area, porosity, and adsorption capacity. However, these properties can be improved. Therefore, modifications can be made through the activation of biochar, which can be physical or chemical. In activation, the objective is to open the pores, to obtain one of a biochar with larger volumes and pore diameters, a better distribution of pore size. In addition, activation can provide more active and available adsorption sites, greater mass transfer capacity, and increased active loading surface for catalysis process [30, 48, 49]. Figure 1 shows an image obtained by Scanning Electron Microscope (SEM) of a biochar based on orange peel in a), and the same after undergoing an activation process in b) [50].

In physical activation, also called thermal activation, the material is subjected to a heat treatment, and can be in a current usually containing an inert gas. This process can also be conducted under vacuum conditions or in an oxidizing/reducing atmosphere. Physical activation occurs in two steps, first a carbonization, followed by gasification [51]. In this process, the material is subjected to temperatures ranging between 600 and 900 °C. First, the less stable chemical bond is broken, forming radical species. These species are easily stabilized with additions of hydrogen, thus promoting the formation of volatile compounds on the surface of the material. Then, at the highest temperatures, the rings condense to form carbon domains sp^2, generating more empty spaces and modifying the structure of the functional groups present [52–54].

Chemical activation, in general, is performed by impregnating the lignocellulosic precursor with a chemical agent, and the impregnated material will be carbonized. After the process, the activating agent is removed through washes so that pH is around neutrality. Some examples of activating agents, commonly used in the chemical activation of biochar, are: H_3PO_4; NaOH; KOH; $ZnCl_2$ and $FeCl_3$ [41, 44, 45]. After carbonization, the activating agent is housed between the layers of the sp^2 carbon

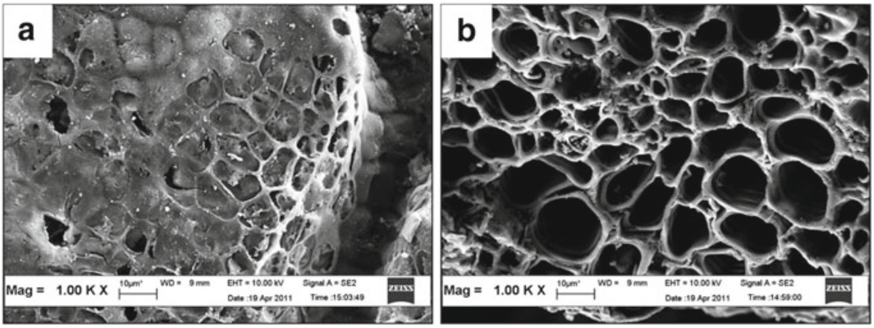


Fig. 1 SEM images of a biochars of orange peel: **a**) no activated; **b**) activated [50]

domains, which is expanded, in which after washing the material with an appropriate solution, promotes the formation of the homogeneous microporous structure. This activation usually occurs at lower temperatures when compared to physical activation, promoting higher yields of biochar [53, 57].

4 Clays

Clays and clay minerals have been materials used since the dawn of humanity [58–60]. They are increasingly used in countless applications such as fertilizers, catalysts, foundry sands, refractory bricks, adsorbents, bleaching, and clarifying agents for oils and fats, paints, filtering agents, fillers for polymers and elastomers, paper, etc. [61, 62]. This is due to the variety of existing clays and the properties that these materials present, such as swelling, adsorption, plasticity, and rheological and colloidal properties [63]. The use of clay minerals has received much attention as effective adsorbents for organic and inorganic pollutants in wastewater [64].

Historically, the term clay refers to small inorganic particles in the $< 2\ \mu m$ portion of a soil fraction, regardless of composition or crystallinity. Clay minerals refer to the specific phyllosilicates (the term for sheet silicate structures), the layered, hydrating, magnesium, or aluminum silicates in such a fraction [61]. Table 4 presents the distinction between clay and clay minerals [65].

Due to intrinsic characteristics and properties, clay minerals appear as excellent low-cost materials for minimizing surface water pollution, mainly by adsorption, and can be synthesized and adapted to meet specific needs [66–68].

4.1 Structure

Clay minerals are hydrated phyllosilicates known as "leaf silicates" and are distinguished by their layered structure. Tetrahedral and octahedral sheets form the basic mineralogical structure of the phyllosilicate layers. The regular tetrahedral sheet consists of each silicon atom coordinating with four oxygen atoms. These silicon cations are linked through covalent bonds through shared oxygens and are arranged as

Table 4 Distinction between clay and mineral

Clay	Clay mineral
Natural	Natural and synthetic
Fine-grained ($< 2\ \mu m$ or $< 4\ \mu m$)	No size criterion
Phyllosilicates as principal constituents	May include non-phyllosilicates
Plastic	Plastic
Hardens on drying or firing	Hardens on drying or firing

a hexagonal lattice along this basal plane. Octahedral sheets are generally composed of aluminum, magnesium, or iron atoms and are coordinated by a compact arrangement of six oxygen atoms or hydroxyl groups in an octahedral configuration. These octahedrons are linked through shared edges forming sheets with a hexagonal or pseudo-hexagonal pattern [69–71].

Silicon and aluminum, the most abundant chemical elements in the earth's crust after oxygen, are the predominant cations at tetrahedral and octahedral sites, respectively [72]. There are cases where Al^{+2} can replace Si^{+4} in the tetrahedral sheet, causing a negative charge on the sheet. However, this substitution is relatively small, occurring at levels of up to 25% in micas. Occasionally Fe^{+3} ions can also be found in tetrahedral sheets. More cation variation is found in the octahedral layers. Cations such as Fe + 3, Fe^{+2}, Mg^{+2}, and occasionally Mn^{+2}, Ni^{+2}, Li^{+1}, Zn^{+2}, Cu^{+2}, Cr^{+3}, and titanium are identified octahedral sites. Isomorphic substitutions for higher charged cations, the most common substitution, leave the negative charge on these octahedral sheets. In dioctahedral minerals, the most common substitution is Mg^{+2} for Al^{+2} and Li^{+1} for Mg^{+2} in trioctahedral minerals [61, 72].

The wide variety of clays found in nature is due to the numerous substitutions that can occur at locations in tetrahedral and octahedral sheets, as the characteristics of the outer surface and the interlamellar region are altered during these ion exchange processes [65, 69]. There are two basic layering arrangements based on the proportion of tetrahedral and octahedral sheets in clay minerals, which gives the classification for these phyllosilicates.

The free oxygen, known as apical oxygen (Oa), of all tetrahedrons, is disposed to the same side of the sheet and is responsible for forming a common plane with an octahedral anionic position, coming from the connection of the tetrahedral and octahedral sheets. The 1:1 layer structure consists of the repetition of a tetrahedral sheet and an octahedral sheet, while in the 2:1 layer structure, an octahedral sheet is intercalated between two tetrahedral sheets [61, 73, 74]. These materials can be modified to improve intrinsic characteristics and be synthesized and adapted to meet specific needs [66, 67].

4.2 Modified Clay Minerals for Environmental Applications

Heat Treatment–Thermal activation

Exposure of clay minerals to heat treatment can significantly alter the properties of the clay. These natural materials may contain water adsorbed on their surface or in the voids between their particles, causing mechanical resistance, viscosity, or plasticity in aqueous solution systems. The alteration in the materials occurs mainly by the redistribution of hydrated cationic species in the intermediate clay layers and dehydroxylation of the silanol and aluminol groups of the clay [75, 76].

Heat treatment of clay minerals can also change the pore size distribution and surface area of clay minerals. Changes in structure prevent the material from dissolving in aqueous media and increase mechanical strength and adsorption capacity [77].

Acid Treatment

One of the most common chemical modifications in clays used for industrial and scientific purposes is their acid activation. The acid activation process alters the material's physical properties, chemical composition, and crystalline structure, increasing the specific area, apparent porosity, and surface acidity [78]. This process is usually done with strong acids such as sulfuric acid (H_2SO_4) or hydrochloric acid (HCl). Temperature, reaction time, and acid concentration are the control variables for obtaining activated mineral clay, and the values of these variables may vary from one mineral clay to another [79].

During the activation process, the acid exchanges its protons for the clay cations, partially dissolving the existing crystalline structure. In addition, the acid treatment can dissolve some impurities in the material, being one of the factors that help improve the properties of clays and increase the adsorption capacity [73, 79, 80]. At the end of the acid treatment process, the activated clay must be washed until there is no free acid on the material's surface, ensuring that the surface acidity does not have a trace of free acid [80].

Organoclay Minerals

Organic clays are prepared by the intercalation of organic molecules in the clay mineral structure. This intercalation presents particularities according to the types of organic compounds [81]. The binding mechanism between the organic cation and the charged mineral clay layers is electrostatic, but other forces may contribute to the adsorption of these cations. The attraction by the Van der Waals force between organic species and the clay mineral surface, as well as between adjacent organic species themselves, increases the adsorption forces [61]. Some organic molecules exchange with hydrated cations in the interlamellar space of the clay mineral and do not become adsorbed on its surface. The length of these alkyl chains can vary, increasing the level of complexity and hydrophobicity of the molecule.

A clay mineral is hydrophilic due to the hydrated cations in the interlamellar layer. The hydrated cations can be replaced by organic cations of a hydrophobic nature, making the resulting clay mineral organophobic. Thus, the new material interacts differently concerning contaminants compared to the parent clay. An essential consideration in selecting striker clay for the preparation of organic clay is its expansive nature. An expansive clay mineral would be able to intercalate the organic molecules into its interlayer structure, while others would adsorb the organic molecules as just an outer surface coating. The adsorption isotherms show that for large cations, Van der Waals forces dominate since the main interaction is between the adsorbed organic species themselves and not between the organic species and the clay surface [61]. The adsorption of organic cations depends on the pH of the solution. For cations to be the dominant species in the solution, the pH must be lower than the pK. If the medium is too acidic, adsorption may be impaired due to competition with H^+ ions or metal cations released from the precursor network due to an acid attack. Adsorption will also depend on the solubility of the base in water, which in turn may be pH-dependent [62, 82].

Pillared Clay Minerals

Pillared clays form a class of materials that have chemical species interspersed in the interlamellar space, giving them a highly porous structure with good thermal stability, greater hydrophobicity, and improved strength [83]. The most common procedure for obtaining a pillared clay mineral can be summarized in the following steps: swelling of the clay mineral in water or another polar solvent; exchange of natural interlamellar cations for cationic oligomers of the metal of interest; drying and calcination of the intercalated material to transform the metal species into oxides, acting as pillars and keeping the lamellae apart. Pillared clay minerals can undergo hydration and dehydration without harming their porosity [73, 83]. The following criteria must be met for a pillared clay material to be considered produced [61, 84].

- The minimum increase in basal spacing is equal to the diameter of the N_2 molecule, commonly used to measure surface areas and pore volumes.
- The layers are vertically separated and do not collapse with solvent removal.
- The pillaring agent has molecular dimensions and is laterally spaced on a molecular length scale.
- The interlamellar space is porous. The minimum pore opening size is the diameter of the N_2 molecules, and there is no upper limit to the pore size.

An organic or inorganic compound, known as a pillaring agent, is sandwiched between adjacent layers of clay material. Inorganic agents, essentially oligomers, are more common than organic agents. The characteristics of pillared clays can be controlled and adjusted according to the pillaring agent. In addition, the new material is named according to the host clay mineral and pillaring agent [83, 85].

The pillared clays have Brønsted acidity and Lewis's acidity, the first being associated with the hydroxyl groups of the structure. In contrast, the second is attributed to the metal constituting the pillar. There is acidity at the edges of the clay minerals particles, being related to the acidity of both Brønsted and Lewis [86, 87].

Surfactant Treatment

Over time, surfactants began to be used to change the properties of clays and improve their adsorption capacity. Surfactants are organic compounds that have polar and nonpolar characteristics and are usually classified based on their dissociation in water into cationic, anionic, and non-ionic surfactants. The main objective of the intercalation of surfactant ions in the structure of the clay mineral is to transform hydrophilic surfaces into hydrophobic ones, and the extent of these modifications depends on the structure of the layers, the degree of swelling of the clays, the molecular size and the functional groups of the surfactant used [73, 88]. The main cationic surfactants are alkylammoniums and alkylamines (salts of fatty amines and quaternary ammonium). Some of the main anionic surfactants are soaps, lauryl sulfate, sulfosuccinate, etc.

Non-ionic surfactants are not dissociative in water, such as amines, fatty acid esters, and ethoxylated linear alcohols, among others.

The surface modification of clay minerals with cationic surfactants involves the process of cation exchange and the binding of the hydrophobic part in the layers of the material. The interlamellar spacing undergoes expansion due to the action of the surfactant, displacing the ions on the clay surface [64, 89–91]. In addition, the hydrophobicity, oleophilicity, basal spacing, particle size, and thermal properties of the modified materials strongly depend on the alkyl chain length and functional groups of the surfactants [73, 92]. Although anionic surfactants are cheaper and have many industrial applications, they are rarely used to modify clay minerals. Non-ionic surfactants present advantages compared to cationic and anionic surfactants, presenting better thermal and chemical stability, being biodegradable and non-toxic, offering the preservation of exchangeable inorganic cations after adsorption, and having the possibility of exchanging cations with organic and inorganic cations [73, 93–95].

Over time, a new group of surfactants was created. Gemini surfactants, also known as dimeric or biosurfactants, comprise molecules with two hydrophilic groups in the head and two hydrophobic groups in the tail, chemically connected by a rigid or flexible spacer, covalently bonded. Gemini surfactants can be divided into cationic, anionic, non-ionic, and zwitterionic. They have advantages over conventional surfactants, such as water solubility, high thermal stability, differentiated aggregation and phase behavior, antimicrobial activity, and excellent surface/interfacial and rheological properties [73, 96, 97].

5 Composites: Synthesis and Characteristics

Recent studies show that clay minerals, biochar, and activated carbon are the main types of adsorbents for aqueous matrices and industrial effluents [98–101]. However, despite technological advances, clay minerals with only one modification hardly meet the requirements of real effluent treatment systems due to many pollutants in only one matrix [102]. From these observed limitations, studies on clay composites began [103, 104]. By definition, composites are solid materials resulting from combining two or more simple materials that develop a continuous phase [105]. The physical and chemical properties that make clay minerals interesting are particle size, surface chemistry, particle shape, and surface area. Due to their lamellar structure and high ability to perform ion exchange, clay minerals have the potential to fix several pollutants, including heavy metals, dyes, emerging pollutants, and organic compounds [106]. Clay composites have received attention for presenting properties and performance superior to their components [107–109]. In addition, clay composites can be treated with a combination of modification methods. According to the type of material and modification, composites can be classified into three categories: clay-carbon material composites, organoclay, and silicate-clay hybrids [102, 110].

Some methods, such as surface modification, have been used to create clay-carbon material composites (biochar-based materials), thus having their functions improved. The biochar acts as porous support for the composite, maintaining the distribution of mineral particles within the structure. Thus, the composite combines the sorption abilities of the two materials, having the adsorption capacity governed by the source of the biomass and the activation conditions of the materials, which ends up allowing the adsorption of a greater range of contaminants [102, 111]. Therefore, studies of the composite with clay minerals are studied to optimize their use, allowing the use of their adsorptive characteristics. These composites have promising applications in treating heavy metals, dyes, phenolic compounds, and ammonia [112–115]. In general, the most used types of synthesis of biochar/clay composites can be classified into two groups: pre-treatment methods and post-treatment methods.

In pre-treatment methods, the biochar raw material is immersed in a clay mineral suspension, before the pyrolysis process occurs, this process will lead to the formation of a biochar with mineral particles on its surface after pyrolysis [116–119]. The post-treatment method consists of impregnating the biochar that has been previously prepared with a clay solution [120–122].

The synthesis of the composite biochar/LDH can take place in one or more steps, depending on whether the mixing of metal cations will occur before or after the carbonization process. In general, when the step of mixing the metallic precursors takes place before pyrolysis, the raw material and the metallic salts are mixed in an aqueous solution and subjected to high temperatures. However, most of the biochar/LDH composites are prepared through the liquid phase deposition process, which consists of preparing the biochar using any of the methods, then putting it in contact with the metallic cations in the appropriate proportions to formation of LDH [9, 123].

Hydrothermal carbonization is a method that can also be used for composite synthesis. Hydrothermal conversion is the transformation of biomass in a single step to create a nanocomposite. In this process, a mixture is prepared that contains the raw material for the production of biochar, as well as the metallic salts that form the LDHs in a previously defined proportion, later, the pH is adjusted and the mixture is then placed in an autoclave and heated until the formation of the composite [124]. In the spontaneous self-assembly method, mixed metal solutions have the pH adjusted to 10 and together with the biochar it goes to age in the oven for a few days at a suitable temperature, then the material passes through filter paper, is washed with deionized water and dried [125]. Another alternative to produce biochar/LDH composites is pyrolysis assisted by electric field. This method consists of generating an electrochemical cell using the mixture of biochar with metal hydroxides, under constant agitation and acid pH, passing a current for a short period over time. This process generates a material containing a larger porous surface and a more uniform distribution of LDH [126]. A summary of the methods cited can be seen in Fig. 2.

Biochar/clay composites can also be synthesized by the method known as adsorption-pyrolysis, where the natural raw material together with the precursor of metallic cations is suspended in a basic medium. The main differences in this method are the presence of an aging step, as well as a drying, before the pyrolysis takes place under N_2 atmosphere at a suitable temperature [127]. A similar method

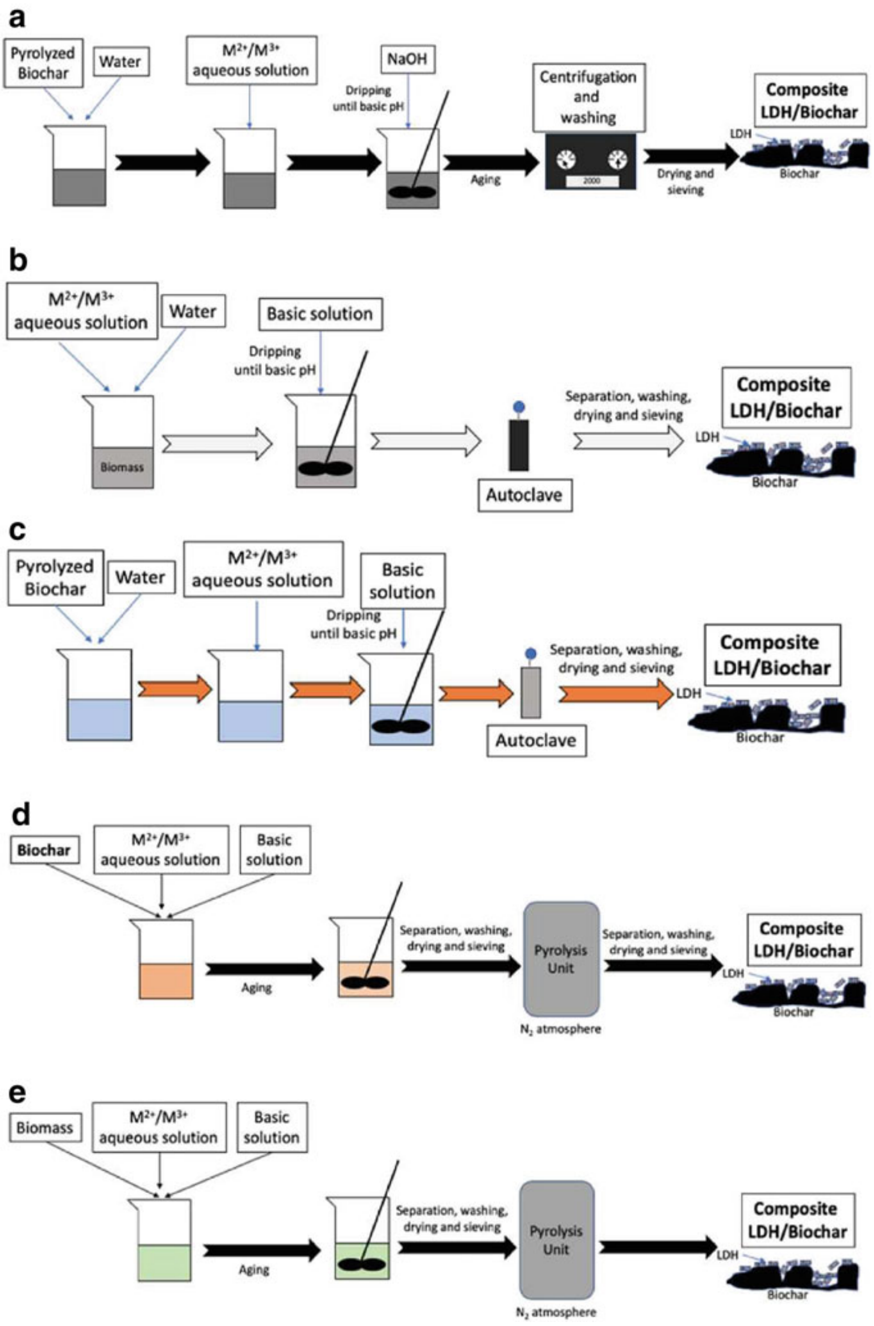


Fig. 2 Scheme of biochar/LDH synthesis by methods of **a** liquid phase deposition; **b** hydrothermal carbonization; **c** hydrothermal synthesis; **d** adsorption-pyrolysis method; **e** coprecipitation + heat treatment [4]

cited in the literature consists of the initial stable suspension of clays, in this case montmorillonite and kaolinite, followed by sonication. The biochar raw material is then dipped in the clay suspension and stirred for a while, then it is dried in an oven. Finally, the mixture of raw material and clay is deposited in a quartz tube inside a tubular oven to produce composites through slow pyrolysis [106].

Studies on clay-polymer composites have expanded progressively in recent years [128, 129]. The composite consists of a material with at least one of the existing phases in a nanometric dimension, less than or equal to 100 nm [73]. The incorporation of clay minerals increases the adsorption capacity and provides mechanical and thermal stability to the polymer matrix. There are three main methods for preparing clay-polymer [73, 130, 131]:

- Interleaving by melting: the polymer and clay mineral are mixed and melted in a melting chamber under controlled conditions of temperature, shear, and residence time;
- In situ polymerization: involves the incorporation of the polymer into the interlamellar space of the clay mineral through the action of an initiator;
- Solvent extraction: the polymer is added to the dispersed clay mineral solution, which can dissolve the polymer. Intercalation occurs within the mineral clay layers, and the nanocomposite is produced after solvent removal.

The third class of composite is the clay-silicate composite, where this inorganic-inorganic hybrid material is considered a promising strategy due to its compatibility and stability characteristics [102, 104]. Due to its non-toxicity, the hybrid composite has drawn attention to removing heavy metals and dyes [132–134].

6 Adsorption of Pollutants

6.1 Mechanism of Adsorption

Proposing interaction mechanisms in adsorptive processes is not trivial. For cation adsorption, the pH value of the solution infers about the way in which the cations will be available to interact. Basic means favor the formation of precipitates of metal cations in the form of hydroxides, or even, can form soluble complexes. In acidic media, these metallic cations tend to be in free form, thus favoring electrostatic type interactions between cation and adsorbent.

For organic pollutants, the pH value of the medium can affect the chemical form as the organic pollutant is found in the solution, thus directing the direction of the balance between its molecular and ionic form. Moreover, molecular species are susceptible to protonation, when in solution with higher concentrations of H_3O^+, or deprotonation, when in solutions with concentrations of OH^- in a majority form. In addition to pollutants, the pH of the medium also interferes with the adsorbent surface.

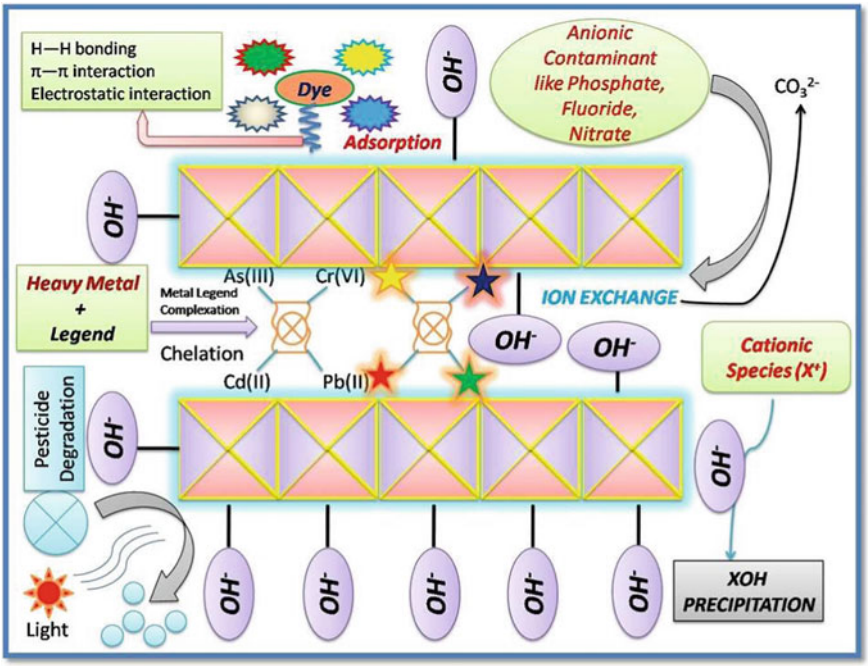


Fig. 3 Types of interactions between lamellar clays and inorganic and organic species. *Source* [138]

Clays, for example, due to their characteristic layered structure, as well as the various possibilities of synthesis, can interact with organic and inorganic species by different routes. Thus, we highlight: ion exchange, quelation, surface complexation, precipitation, and isomorphic substitution, as can be observed in Fig. 3 [135–137].

In clays, adsorption mechanisms via precipitation were proposed in the studies by González et al. [140] and Rojas [139] [128, 129]. Yang et al. [141] suggested interactions of the superficial complexation type and precipitation in the adsorption of Pb^{2+} ions with modified LDH/MgAl [141]. In their studies, Chen et al. [128] synthesized LDH-MgAl interspersed with EDTA for removal of Cu ions in solution, attributing the mechanism to EDTA quelation. In addition, adsorbent regeneration was performed using Na_2CO_3 [142].

In biochar, the presence of C−H, C−O−H, C = O, and C = C connections, derived from the raw material of origin after the pyrolysis process, is expected. In addition, nitrogen, sulfur, and halogen atoms may be associated. This variety of species impacts the adsorptive process due to electrostatic, metal-π, π-π and Van der Waals forces, in addition to oxide-reduction, precipitation, complexation, and ion exchange reactions [143–145].

Acid and basic groups, such as carboxylics, amines, phenolics, quinones, and lactone, confer more polar characteristics, making the biochar surface more

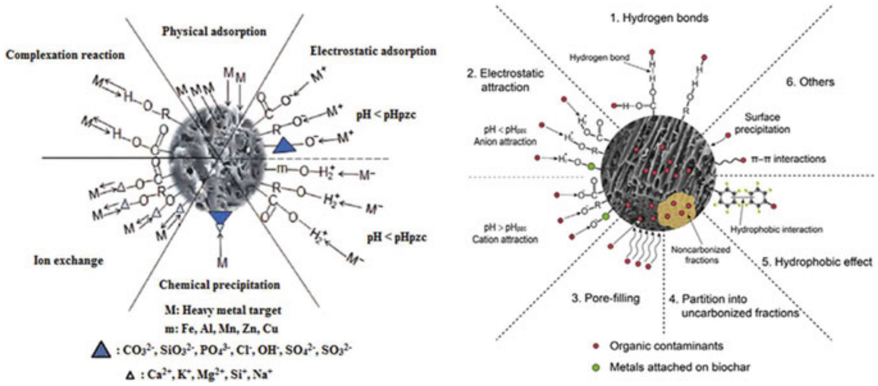


Fig. 4 Types of interactions on biochar in adsorption processes. *Source* Adapted [149]

hydrophilic, with a tendency to interact with polar and ionic species. The surface load of the biochar is influenced by the presence of these groups and the pH of the solution. Similarly, nonpolar groups of type C−H, C–C, and C = C favor the adsorption of nonpolar organic contaminants [143, 146–148]. Figure 4 shows some types of interactions that can occur in biochar in adsorption processes.

Adsorption also stands out for the possibility of combining adsorbent materials, to potentiate their adsorptive and morphological properties, for the removal of inorganic or organic pollutants. In view of this, composites consisting of biochar and clays are promising. In these composites, biochar provides a porous structure that can support micro and clay nanoparticles within the carbonaceous matrix [150–152].

Gao and Goldfarb [147] synthesized a composite showed a strengthening in the aromatic structures of biochars, as well as increases in the superficial functional groups containing oxygen. In addition, the results obtained from adsorption isotherms indicated that the composites had higher adsorption capacities than the isolated biochars. Finally, the adsorption mechanism, with methylene blue, was assigned as hydrogen bonds [153].

6.2 Dyes, Metals, Emergent Pollutants, Pesticides, and Herbicides

Urbanization and industrial growth are sources with great potential for contamination of the environment. The result of these activities, water and soil contamination has become a serious problem, with a great need to develop technologies that are capable of performing wastewater treatment, as well as soil remediation to remove toxic contaminants [154].

The textile industry uses a lot of water during the dye manufacturing process, generating a large amount of effluent that contains dyes, inorganic ions, and wetting agents in its composition. These effluents have high concentrations of heavy metals, acidic properties, dark color, and components that do not readily biodegrade. In this way, the incorrect disposal or leakage of this effluent into the environment can cause serious risks to human health [9, 127].

Due to the development of new techniques for detecting pollutants in water treatment plants, a new class of pollutants has been identified, which are known as emerging pollutants. These pollutants consist of a group of natural or synthetic substances, generally found in low concentrations, harmful to the environment and to humans and, in general, are not included in monitoring routines. In this class of pollutants we can mention: pharmaceuticals, personal hygiene products, pesticides, among others [154–156].

Heavy metals such as As, Pb, Zn, Cu, Ni, and Ag are widely found in natural waters, as well as in effluents, these substances can cause many problems to human health, entering the body through the food chain and causing irreversible damage, that can be transferred to the next generation [157].

The adsorption technique using biochar as an adsorbing agent to remove pollutants in aqueous solution has been enshrined in engineering for some decades, however, works have shown a better performance of biochar when its surface is enriched with clays [106, 158]. An alternative for these types of contaminants is the use of biochar/clay composites, as has already been established in the literature by several researchers. The results of the isothermal experiments indicated that the enrichment of bagasse biochar with montmorillonite greatly increased the adsorption capacity of the ethylene blue dye. Which went from 30.35% removal with the use of pure biochar, to 84.33% with the use of composite [106]. Biochar and clay mineral composites were studied for nitrate removal in aqueous medium, the material resulting from the pyrolysis of rice straw and montmorillonite resulted in a higher percentage of contaminant removal, the composite was able to adsorb 80% more nitrate from the water, when compared to pure biochar [159]. In another study, also with montmorillonite, however, corn husk-based biochar adsorbed approximately 241% more Zn from the water, when compared to pure biochar [160]. Overall, most research results indicate that the adsorptive capacity of biochar increases with the enrichment of the surface with clays. Table 5 presents data from several articles in the literature containing the biochar used, clay, synthesis method and the pollutant removed.

7 Perspective and Future Directions

Currently, in the field of water treatment, the innovation of the research is focused on the exploration of new adsorbents, and its main technological route is the optimization of the material that presents high performance, is multifunctional and low cost. Among these approaches, adsorption using clay/BC composites has been widely used as the most preferred approach for the removal of different contaminants.

As emphasized in this chapter, clay/BC composites have fascinating characteristics due to their sustainable nature, low cost, and potential to efficiently remove many

Table 5 Articles in the literature containing the biochar used, clay, synthesis method, and the pollutant removed

Raw material	Clays	Synthesis	Adsorbate	Reference
Bamboo	Montmorillonite	adsorption-pyrolysis	Methylene Blue	[106]
Bamboo	Kaolinite	adsorption-pyrolysis	Methylene Blue	[106]
Berry	Montmorillonite	adsorption-pyrolysis	Methylene Blue	[106]
Berry	Kaolinite	Adsorption-pyrolysis	Methylene blue	[106]
Hickory chips	Montmorillonite	Adsorption-pyrolysis	Methylene blue	[106]
Hickory chips	Kaolinite	Adsorption-pyrolysis	Methylene blue	[106]
Wheat straw	MgFe	Coprecipitation	Nitrate	[161]
Rami (*Boehmerianivea*)	MgAl	Co-pyrolysis	Violet crystal	[127]
Wood Pine	Nife	Co-pyrolysis	As (V)	[125]
Wood Pine	Nife	Coprecipitation	As (V)	[125]
Husk Rice	MgFe	Coprecipitation	Pb (II)	[162]
Camellia oil-tea shells	MgFe	Hydrothermal	Pb (II)	[163]
Caraganakorshinskii	MgAl	Electro-assisted	Phosphate	[164]
Tobacco stalk	MgAl	One hydrothermal step	Phosphate	[165]
Banana straw	ZnAl	Hydrothermal	Phosphate	[166]
Husk Rice	MgAl	Co-pyrolysis	Phosphate	[167]
Bamboo	MgAl	Co-calcination	Cr (IV)	[168]
Bone bovine	MgAl	Coprecipitation	Methylene blue	[9]
Bone bovine	MgAl	Coprecipitation	Caffeine	[154]
Corn straw	Montmorillonite	Hydrothermal	Zn	[160]
Bone bovine	MgAl	Coprecipitation	Diclofenac	[169]

toxic pollutants [4]. However, for the effective application of composites there are still some limitations and gaps present in the ongoing research highlighted below.

The detailed study of the structure and surface of composites is imperative to expand their applications since the incorporation of different materials can overcome the limitations of pure materials. Many works produce composites of this class, but do not highlight the synergistic effect of the composition and what benefits are acquired from the formation of the composite. For example, Fang et al. (2021) cite that BC have limited adsorption of oxyanions, such as phosphate ions (P), and are difficult to disperse in solution [170]. Thus, the functionalization of BC with a clay is required to supply this deficiency, as in the case of HDLs that can adsorb several types of oxyanions, among the phosphate. Therefore, it is understood that without this preliminary assessment there is no purpose in merging the two materials.

In this direction, the attention of the research should be based in the study of the characteristics of the pure components and of the composites. For this purpose, a detailed characterization capable of revealing its textural, structural, morphological, and chemical characteristics is required before being used in some adsorptive process, in order to know and understand the adsorption/desorption processes that occur when submitted to contact with contaminants.

This point converges with the need to expand the coverage of pollutants that these adsorbents can effectively treat. It is imperative to search for advanced functionalized materials that can cover a wide range of pollutants. Many works produce the composite and prepare one or some solutions with certain pollutants and discuss the adsorption of these pollutants, without making inferences to the others that are abundantly available in real waters or do not study the effect of the interfering pollutant. There are still few works that demonstrate the application of clay/BC composites for the removal of pollutants from real waters. It is important to expand this field of research and evaluate adsorption mechanisms in practical applications [171].

Another line of research, with great potential for exploration, is to produce multifunctional composites with the ability to treat various types of pollutants simultaneously. For this, more than one type of BC or clays can be tested in the same composite. With the purpose of increasing, mainly, the number of functional groups to increase the removal efficiency of potentially toxic elements.

It is also worth mentioning the importance of determining the fraction of each component of the composites. Interestingly, in many works, the composites are produced in a fixed composition and remain fixed throughout the batch of experiments and no details are given about the determination of the amount of clay and biochar in the composite. It is necessary to optimize the proportion of clay or BC in the composite so as not to employ an excess amount of the more expensive or less active material in the adsorption process.

However, for the effective use of clay/BC composites as an adsorbent, a study on their production on an industrial scale is required. The specific literature is still silent on this topic; many works are limited to bench tests without mentioning the challenges of designing bench tests for an industrial level production. This industrial feasibility is also linked to a cost analysis; although BCs are produced from residual biomass and the synthesis of clays is easily synthesized, there is a cost associated with converting materials into adsorbents.

Thus, it is urgent to improve or develop an economical method for the mass production of clays, biochars and their composites. Therefore, alternative methods need to be explored. More recent articles already mention more modern production methods. To produce biochar, microwave-assisted pyrolysis, steam activation-assisted pyrolysis, co-pyrolysis, hydrothermal and flash carbonization, roasting and gasification can be mentioned as alternatives [171, 172]. While for clays, more modern microwave and ball milling techniques can be mentioned, used, for example, in the production of LDHs [173].

Finally, it is also important to highlight that there is limited data on studies of regeneration and reuse of composites in real water**.** Linked to this, there is the problem of elimination of clay after its use. Fang et al. [170] highlight that BC/LDH composites used as adsorbents for P-contaminated water could be used as fertilizers in agriculture, but that there are no studies to explore this theme [170]**.**

The field of analysis of clay/BC composites is wide, and other factors besides those mentioned in this text, which must be analyzed in the specific case, must be considered. In general, it can be assumed that advanced research encompassing the selection of raw materials, characterization, conversion techniques, optimization of synthesis parameters to produce BCs, clays and their composites should be considered in the future.

References

1. Hacıosmanoğlu, G.G., Mejías, C., Martín, J., Santos, J.L., Aparicio, I., Alonso, E.: Antibiotic adsorption by natural and modified clay minerals as designer adsorbents for wastewater treatment: A comprehensive review. J. Environ. Manage. **317**, 115397 (2022). https://doi.org/10.1016/J.JENVMAN.2022.115397
2. Hnamte, M., Pulikkal, A.K.: Clay-polymer nanocomposites for water and wastewater treatment: A comprehensive review. Chemosphere **307**, 135869 (2022). https://doi.org/10.1016/J.CHEMOSPHERE.2022.135869
3. Iravani, R., An, C., Adamian, Y., Mohammadi, M.: A review on the use of nanoclay adsorbents in environmental pollution control, (123AD). https://doi.org/10.1007/s11270-022-05580-2
4. dos Santos, G.E.D.S., dos Santos Lins, P.V., de Magalhães Oliveira, L.M.T., da Silva, E.O., Anastopoulos, I., Erto, A., Giannakoudakis, D.A., de Almeida, A.R.F., da Silva Duarte, J.L., Meili, L.: Layered double hydroxides/biochar composites as adsorbents for water remediation applications: recent trends and perspectives, J. Clean. Prod. **284** (2021) 124755. https://doi.org/10.1016/j.jclepro.2020.124755.
5. Alsawy, T., Rashad, E., El-Qelish, M., Mohammed, R.H.: A comprehensive review on the chemical regeneration of biochar adsorbent for sustainable wastewater treatment, (n.d.). https://doi.org/10.1038/s41545-022-00172-3
6. Zhang, X., Zhang, L., Li, A.: Eucalyptus sawdust derived biochar generated by combining the hydrothermal carbonization and low concentration KOH modification for hexavalent chromium removal. J. Environ. Manage. **206**, 989–998 (2018). https://doi.org/10.1016/J.JENVMAN.2017.11.079
7. Wang, S., Gao, B., Li, Y., Wan, Y., Creamer, A.E.: Sorption of arsenate onto magnetic iron–manganese (Fe–Mn) biochar composites. RSC Adv. **5**, 67971–67978 (2015). https://doi.org/10.1039/C5RA12137J
8. Wang, S., Gao, B., Li, Y.: Enhanced arsenic removal by biochar modified with nickel (Ni) and manganese (Mn) oxyhydroxides. J. Ind. Eng. Chem. **37**, 361–365 (2016). https://doi.org/10.1016/j.jiec.2016.03.048
9. Meili, L., Lins, P.V., Zanta, C.L.P.S., Soletti, J.I., Ribeiro, L.M.O., Dornelas, C.B., Silva, T.L. and Vieira, M.G.A.: MgAl-LDH/Biochar composites for methylene blue removal by adsorption, Appl. Clay Sci. **168**, 11–20(2019). https://doi.org/10.1016/j.clay.2018.10.012
10. Santos, G.E., Ide, A.H., Duarte, J.L.S., McKay, G., Silva, A.O.S., Meili, L.: Adsorption of anti-inflammatory drug diclofenac by MgAl/layered double hydroxide supported on Syagrus coronata biochar. Powder Technol. **364**, 229–240 (2020). https://doi.org/10.1016/j.powtec.2020.01.083
11. Vanessa, P., Lins, S., Carlos, D., Honjo, A., Leandro, J., Luiz, G., Yazidi, A., Erto, A., Lucia, C., Paiva, D., Zanta, S., Meili, L.: Adsorption of a non-steroidal anti-inflammatory drug onto MgAl / LDH- activated carbon composite—Experimental investigation and statistical physics modeling, Colloids Surfaces A. **586**, (2020). https://doi.org/10.1016/j.colsurfa.2019.124217.

12. Wang, S., Gao, B., Li, Y., Mosa, A., Zimmerman, A.R., Ma, L.Q., Harris, W.G., Migliaccio, K.W.: Adsorptive removal of arsenate from aqueous solutions by biochar supported zero-valent iron nanocomposite: Batch and continuous flow tests. Bioresour. Technol. **22**, 239–245 (2015). https://doi.org/10.1016/j.jhazmat.2016.01.052
13. Zhao, L., Cao, X., Mašek, O., Zimmerman, A.: Heterogeneity of biochar properties as a function of feedstock sources and production temperatures. J. Hazard. Mater. **256–257**, 1–9 (2013). https://doi.org/10.1016/j.jhazmat.2013.04.015
14. Parvej, A.M., Rahman, M.A., Reza, K.M.A.: The combined effect of solar assisted torrefaction and pyrolysis on the production of valuable chemicals obtained from water hyacinth biomass. Clean. Waste Syst. **3**, 100027 (2022). https://doi.org/10.1016/j.clwas.2022.100027
15. Subagyono, R.D.J.N., Miten, P.D., Sinaga, R.J., Wijayanti, A., Qi, Y., Marshall, M., Sanjaya, A.S., Chaffee, A.L.: Pyrolysis of fast growing wood Macaranga gigantea: Product characterisation and kinetic study. Fuel **315**, 123182 (2022). https://doi.org/10.1016/j.fuel.2022.123182
16. Gao, X., Tan, M., Jiang, S., Huang, Z., Li, C., Lei, T., Wang, Z., Zhu, Y., Li, H.: Pyrolysis of torrefied rice straw from gas-pressurized and oxidative torrefaction: Pyrolysis kinetic analysis and the properties of biochars. J. Anal. Appl. Pyrolysis. **157**, 105238 (2021). https://doi.org/10.1016/j.jaap.2021.105238
17. Farias, R.O., Lins, P.V.S., Gabriel, R., Silva, A.D.R., Carvalho, L.L.M., Meili, L., Albuquerque, A.A., Carvalho, S.H.V., Soletti, J.I., Bispo, M.D.: Pyrolysis of coconut inflorescence wastes: production, effects of parameters, characterization and optimization of phenolic-rich bio-oil. Int. J. Environ. Res. **16**, 1–15 (2022). https://doi.org/10.1007/s41742-022-00393-x
18. Arenas Castiblanco, E., Montoya, J.H., Rincón, G.V., Zapata-Benabithe, Z., Gómez-Vásquez, R., Camargo-Trillos, D.A.: A new approach to obtain kinetic parameters of corn cob pyrolysis catalyzed with CaO and CaCO3. Heliyon. **8**, e10195(2022). https://doi.org/10.1016/j.heliyon.2022.e10195
19. Gan, Z., Zhuang, X., Cen, K., Ba, Y., Zhou, J., Chen, D.: Co-pyrolysis of municipal solid waste and rice husk gasification tar to prepare biochar: An optimization study using response surface methodology. Fuel **330**, 125574 (2022). https://doi.org/10.1016/j.fuel.2022.125574
20. Dai, Q., Liu, Q., Yılmaz, M., Zhang, X.: Co-pyrolysis of sewage sludge and sodium lignosulfonate: Kinetic study and methylene blue adsorption properties of the biochar. J. Anal. Appl. Pyrolysis. **165**, 105586 (2022). https://doi.org/10.1016/j.jaap.2022.105586
21. Tian, X., Wang, K., Shan, T., Li, Z., Wang, C., Zong, D., Jiao, D.: Study of waste rubber catalytic pyrolysis in a rotary kiln reactor with spent fluid-catalytic-cracking catalysts. J. Anal. Appl. Pyrolysis. **167**, 105686 (2022). https://doi.org/10.1016/j.jaap.2022.105686
22. Dai, L., Zhou, N., Lv, Y., Cheng, Y., Wang, Y., Liu, Y., Cobb, K., Chen, P., Lei, H., Ruan, R.: Pyrolysis technology for plastic waste recycling: A state-of-the-art review. Prog. Energy Combust. Sci. **93**, 101021 (2022). https://doi.org/10.1016/j.pecs.2022.101021
23. Feng, S., Zhang, G., Yuan, D., Li, Y., Zhou, Y., Lin, F.: Co-pyrolysis of paper mill sludge and textile dyeing sludge with high calorific value solid waste: Pyrolysis kinetics, products distribution, and pollutants transformation. Fuel **329**, 125433 (2022). https://doi.org/10.1016/j.fuel.2022.125433
24. Demirbaş, A.: Biomass resource facilities and biomass conversion processing for fuels and chemicals. Energy Convers. Manag. **42**, 1357–1378 (2001). https://doi.org/10.1016/S0196-8904(00)00137-0
25. Cortez, L.A.B., Lora, E.E.S., Gómes, E.O.: Biomassa para energia, Editora da UNICAMP, Campinas/SP, (2008)
26. Maia, C.M.B.F., Madari, B.E., Novotny, E.H.: Advances in biochar research in Brazil. Dyn. Soil, Dyn. Plant. **4**, 53–58 (2011)
27. Missio, A.L., Mattos, B.D., Gatto, D.A., De Lima, E.A.: Thermal analysis of charcoal from fast-growing eucalypt wood: Influence of raw material moisture content. J. Wood Chem. Technol. **34**, 191–201 (2014). https://doi.org/10.1080/02773813.2013.852588
28. de Arruda, T.P.M., Pimenta, A.S., Vital, B.R., Lucia, R.M.D., Acosta, F.C.: Evalution of two carbonization routines in rectangular kilns. Rev. Arvore. **35**, 949–955 (2011). https://doi.org/10.1590/S0100-67622011000500020

29. Di Blasi, C., Gonzalez Hernandez, E., Santoro, A.: Radiative pyrolysis of single moist wood particles. Ind. Eng. Chem. Res. **39,** 873–882 (2000). https://doi.org/10.1021/ie990720i
30. Patra, B.R., Mukherjee, A., Nanda, S., Dalai, A.K.: Biochar production, activation and adsorptive applications: a review. Environ. Chem. Lett. **19**, 2237–2259 (2021). https://doi.org/10.1007/s10311-020-01165-9
31. Weber, K., Quicker, P.: Propperties of biochar. Fuel **217**, 240–261 (2018). https://doi.org/10.1016/j.fuel.2017.12.054
32. Fang, Z., Smith, R.L., Jr, Xu, L. eds.: Production of biofuels and chemicals with pyrolysis. Springer Singapore, Singapore, (2020). https://doi.org/10.1007/978-981-15-2732-6
33. Tagliaferro, A., Rosso, C., Giorcelli, M. eds.: Biochar: Emerging applications. IOP Publishing Ltd, London, UK, (2020). https://doi.org/10.1088/978-0-7503-2660-5
34. Ok, Y.S., Uchimiya, S.M., Chang, S.X., Bolan, N. eds.: Biochar: Production, characterization, and applications. Taylor & Francis Group, LLC, (2016)
35. Wang, K., Brown, R.C., Homsy, S., Martinez, L., Sidhu, S.S.: Fast pyrolysis of microalgae remnants in a fluidized bed reactor for bio-oil and biochar production. Bioresour. Technol. **127**, 494–499 (2013). https://doi.org/10.1016/j.biortech.2012.08.016
36. Campanella, A., Harold, M.P.: Fast pyrolysis of microalgae in a falling solids reactor: Effects of process variables and zeolite catalysts. Biomass Bioenerg. **46**, 218–232 (2012). https://doi.org/10.1016/j.biombioe.2012.08.023
37. Bridgwater, A.V.: Principles and practice of biomass fast pyrolysis processes for liquids. J. Anal. Appl. Pyrolysis. **51**, 3–22 (1999). https://doi.org/10.1016/S0165-2370(99)00005-4
38. Jesus, M.S., Martinez, C.L.M., Costa, L.J., Pereira, E.G., Carneiro, A.C.O.: Thermal conversion of biomass: a comparative review of different pyrolysis processe. Rev. Ciência Da Madeira—RCM. **11,** 12–22 (2020). https://doi.org/10.12953/2177-6830/rcm.v11n1p12-22
39. K.J.L. dos Santos, G.E. de Souza dos Santos, Í.M.G.L. de Sá, S.H.V. de Carvalho, J.I. Soletti, L. Meili, J.L. da Silva Duarte, M.D. Bispo, G.L. Dotto, Syagrus oleracea–activated carbon prepared by vacuum pyrolysis for methylene blue adsorption, Environ. Sci. Pollut. Res. (2019). https://doi.org/10.1007/s11356-019-05083-4.
40. Dos Santos, K.J.L., Dos Santos, G.E.D.S., de Sá, Í.M.G.L., Ide, A.H., da Silva Duarte, J.L., de Carvalho, S.H.V., Soletti, J.I. and Meili, L.: Wodyetia bifurcata biochar for methylene blue removal from aqueous matrix, Bioresour. Technol. **293**, (2019). https://doi.org/10.1016/j.biortech.2019.122093
41. Klinger, J.L., Westover, T.L., Emerson, R.M., Williams, C.L., Hernandez, S., Monson, G.D., Ryan, J.C.: Effect of biomass type, heating rate, and sample size on microwave-enhanced fast pyrolysis product yields and qualities. Appl. Energy. **228**, 535–545 (2018). https://doi.org/10.1016/j.apenergy.2018.06.107
42. Ke, L., Wu, Q., Zhou, N., Xiong, J., Yang, Q., Zhang, L., Wang, Y., Dai, L., Zou, R., Liu, Y., Ruan, R., Wang, Y.: Lignocellulosic biomass pyrolysis for aromatic hydrocarbons production: Pre and in-process enhancement methods. Renew. Sustain. Energy Rev. **165**, 112607 (2022). https://doi.org/10.1016/j.rser.2022.112607
43. Aysu, T., Küçük, M.M.: Biomass pyrolysis in a fixed-bed reactor: Effects of pyrolysis parameters on product yields and characterization of products. Energy **64**, 1002–1025 (2014). https://doi.org/10.1016/j.energy.2013.11.053
44. Zhao, B., O'Connor, D., Zhang, J., Peng, T., Shen, Z., Tsang, D.C.W., Hou, D.: Effect of pyrolysis temperature, heating rate, and residence time on rapeseed stem derived biochar. J. Clean. Prod. **174**, 977–987 (2018). https://doi.org/10.1016/j.jclepro.2017.11.013
45. Uddin, M.N., Techato, K., Taweekun, J., Mofijur, M., Rasul, M.G., Mahlia, T.M.I., Ashrafur, S.M.: An Overview of Recent Developments in Biomass Pyrolysis Technologies. Energies **11**, 3115 (2018). https://doi.org/10.3390/en11113115
46. Madhu, P., Livingston, T.S., Kanagasabapathy, H.: Flash Pyrolysis of Lemon Grass (Cymbopogon flexuosus) for Bio-oil Production in an Electrically Heated Fluidized Bed Reactor. Waste and Biomass Valorization. **9**, 1037–1046 (2018). https://doi.org/10.1007/s12649-017-9872-6

47. Akhtar, J., Amin, N.S.: A review on operating parameters for optimum liquid oil yield in biomass pyrolysis. Renew. Sustain. Energy Rev. **16**, 5101–5109 (2012). https://doi.org/10.1016/j.rser.2012.05.033
48. Tang, Z.-E., Lim, S., Pang, Y.-L., Ong, H.-C., Lee, K.-T.: Synthesis of biomass as heterogeneous catalyst for application in biodiesel production: State of the art and fundamental review. Renew. Sustain. Energy Rev. **92**, 235–253 (2018). https://doi.org/10.1016/j.rser.2018.04.056
49. Seow, Y.X., Tan, Y.H., Mubarak, N.M., Kansedo, J., Khalid, M., Ibrahim, M.L., Ghasemi, M.: A review on biochar production from different biomass wastes by recent carbonization technologies and its sustainable applications. J. Environ. Chem. Eng. **10**, 107017 (2022). https://doi.org/10.1016/j.jece.2021.107017
50. Foo, K.Y., Hameed, B.H.: Preparation, characterization and evaluation of adsorptive properties of orange peel based activated carbon via microwave induced K2CO3 activation. Bioresour. Technol. **104**, 679–686 (2012). https://doi.org/10.1016/j.biortech.2011.10.005
51. Panwar, N.L., Pawar, A.: Influence of activation conditions on the physicochemical properties of activated biochar: a review. Biomass Convers. Biorefinery. **12**, 925–947 (2022). https://doi.org/10.1007/s13399-020-00870-3
52. Kwiatkowski, J.F. (ed.): Activated Carbon: Classifications. Nova Science Publishers, New York, Properties and Applications (2012)
53. Heidarinejad, Z., Dehghani, M.H., Heidari, M., Javedan, G., Ali, I., Sillanpää, M.: Methods for preparation and activation of activated carbon: a review. Environ. Chem. Lett. **18**, 393–415 (2020). https://doi.org/10.1007/s10311-019-00955-0
54. Cândido, N.R., Prauchner, M.J., Vilela, A.O., Pasa, V.M.D.: The use of gases generated from eucalyptus carbonization as activating agent to produce activated carbon: an integrated process. J. Environ. Chem. Eng. **8**, 103925 (2020). https://doi.org/10.1016/j.jece.2020.103925
55. Bansal, R.C., Goyal, M.: Activated carbon adsorption, 1st ed. CRC Press, (2005)
56. Prauchner, M.J., Sapag, K., Rodríguez-Reinoso, F.: Tailoring biomass-based activated carbon for CH4 storage by combining chemical activation with H3PO4 or ZnCl2 and physical activation with CO2. Carbon N. Y. **110**, 138–147 (2016). https://doi.org/10.1016/j.carbon.2016.08.092
57. Pallarés, J., González-Cencerrado, A., Arauzo, I.: Production and characterization of activated carbon from barley straw by physical activation with carbon dioxide and steam. Biomass Bioenerg. **115**, 64–73 (2018). https://doi.org/10.1016/j.biombioe.2018.04.015
58. Reddy, D.H.K., Lee, S.M., Kim, J.O.: A review onemerging applications of naturalsericite and its composites. World Appl. Sci. J. **27**, 1514–1523 (2013). https://doi.org/10.5829/idosi.wasj.2013.27.11.1745
59. Rocha, F.N., Suarez, P.A.Z., Guimarães, E.M.: Clays and their applications in pottery and ceramics materials. Rev. Virtual Quim. **6**, 1105–1120 (2014). https://doi.org/10.5935/1984-6835.20140070
60. Acevedo, N.I.A., Rocha, M.C.G., Bertolino, L.C.: Mineralogical characterization of natural clays from Brazilian Southeast region for industrial applications. Ceramica. **63**, 253–262 (2017). https://doi.org/10.1590/0366-69132017633662045
61. Braterman, P.S., Xu, Z.P., Yarberry, F.: Layered double hydroxides (LDHs). In: Auerbach, S.M., Carrado, K.A., Dutta, P.K. (Eds.). Handb. Layer. Mater., 1st ed, p 664. CRC Press, Nova York, (2004)
62. Kloprogge, J.T., Hartman, H.: Clays and the Origin of Life: The Experiments. Life. **12**, 259 (2022). https://doi.org/10.3390/life12020259
63. de Paiva, L.B., Morales, A.R., Díaz, F.R.V.: Organophilic clays: characteristics, preparation methods, intercalation compounds and characterization techniques. Cerâmica **54**, 213–226 (2008). https://doi.org/10.1590/s0366-69132008000200012
64. Awad, A.M., Shaikh, S.M.R., Jalab, R., Gulied, M.H., Nasser, M.S., Benamor, A., Adham, S.: Adsorption of organic pollutants by natural and modified clays: A comprehensive review. Sep. Purif. Technol. **228**, 115719 (2019). https://doi.org/10.1016/j.seppur.2019.115719
65. Bergaya, F., Lagaly, G.: General Introduction: Clays, clay minerals, and clay science. In: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), Handb. Clay Sci. Elsevir Ltd., pp. 1–18 (2006) https://doi.org/10.1016/S1572-4352(05)01001-9

66. de Guimarães, A. M.F., Ciminelli, V.S.T., Vasconcelos, W.L.: Surface modification of synthetic clay aimed at biomolecule adsorption: Synthesis and characterization. Mater. Res. **10**, 37–41 (2007). https://doi.org/10.1590/S1516-14392007000100009
67. Zhang, D., Zhou, C.H., Lin, C.X., Tong, D.S., Yu, W.H.: Synthesis of clay minerals. Appl. Clay Sci. **50**, 1–11 (2010). https://doi.org/10.1016/j.clay.2010.06.019
68. Farias, M.B., Spaolonzi, M.P., Silva, T.L., Silva, M.G.C., Vieira, M.G.A.: Natural and synthetic clay-based materials applied for the removal of emerging pollutants from aqueous medium. In: Giannakoudakis, D.A., Meili, L., Anastopoulos, I. (Eds.), Adv. Mater. Sustain. Environ. Remediat. Elsevier, pp. 359–392 (2022). https://doi.org/10.1016/B978-0-323-90485-8.00012-6
69. Obaje, S.O., Omada, J.I., Dambatta, U.A.: Clays and their industrial applications: Synoptic review. Int. J. Sci. Technol. **3**, 264–270 (2013)
70. Mukherjee, S.: Classification and composition of clay constituents. In: Sci. Clays. Capital Publishing Company, pp. 23–32 (2013). https://doi.org/10.1007/978-94-007-6683-9_2
71. Brigatti, M.F., Galan, E., Theng, B.K.G.: Structures and mineralogy of clay minerals. In: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), Handb. Clay Sci., Elsevier Ltd., pp. 19–86 (2006). https://doi.org/10.1016/S1572-4352(05)01002-0
72. Howard, B.H., Lekse, J.W.: Clay mineralogy. In: Romanov, V. (Ed.), Greenh. Gases Clay Miner. Springer International Publishing AG, pp. 74–81 92019). https://doi.org/10.1016/B978-0-12-813081-0.00186-5
73. Ismadji, S., Soetaredjo, F.E., Ayucitra, A.: Modification of clay minerals for adsorption purpose. In: Clay Mater. Environ. Remediat. SpringerBriefs, pp. 39–56 (2015). https://doi.org/10.1007/978-3-319-16712-1_3
74. Silva Neto, L.D., Anchieta, C.G., Duarte, J.L.S., Meili, L., Freire, J.T.: Effect of Drying on the Fabrication of MgAl Layered double hydroxides. ACS Omega. **6**, 21819–21829 (2021). https://doi.org/10.1021/acsomega.1c03581
75. Silva, M.L.P., Rodrigues, M.G.F., Silva, M.G.C.: Removal of cadmium from thermally activated Toritama (Pernambuco state, Brazil) clay under finite bath conditions. Cerâmica **55**, 11–17 (2009). https://doi.org/10.1590/s0366-69132009000100002
76. España, V.A.A., Sarkar, B., Biswas, B., Rusmin, R., Naidu, R.: Environmental applications of thermally modified and acid activated clay minerals: Current status of the art. Environ. Technol. Innov. **13**, 383–397 (2016). https://doi.org/10.1016/j.eti.2016.11.005
77. Toor, M., Jin, B., Dai, S., Vimonses, V.: Activating natural bentonite as a cost-effective adsorbent for removal of Congo-red in wastewater. J. Ind. Eng. Chem. **21**, 653–661 (2015). https://doi.org/10.1016/j.jiec.2014.03.033
78. Días, F.R.V., Santos, P.S.: Studies on the acid activation of brazilian smectitic clays. Quim. Nova. **24**, 345–353 (2001)
79. Sarkar, B., Rusmin, R., Ugochukwu, U.C., Mukhopadhyay, R., Manjaiah, K.M.: Modified clay minerals for environmental applications. Elsevier Inc., (2018). https://doi.org/10.1016/B978-0-12-814617-0.00003-7
80. Ugochukwu, U.C., Jones, M.D., Head, I.M., Manning, D.A.C., Fialips, C.I.: Effect of acid activated clay minerals on biodegradation of crude oil hydrocarbons. Int. Biodeterior. Biodegrad. **88**, 185–191 (2014). https://doi.org/10.1016/j.ibiod.2013.10.018
81. Sarkar, B., Xi, Y., Megharaj, M., Krishnamurti, G.S.R., Bowman, M., Rose, H., Naidu, R.: Bioreactive organoclay : A new technology for environmental remediation. Crit. Rev. Environ. Sci. Technol. **42**, 435–488 (2012)
82. Hartman, H., Sposito, G., Yang, A., Manne, S., Gould, S.A.C., Hansma, P.K.: Molecular-scale imaging of clay mineral surfaces with the atomic force microscope. Clays Clay Miner. **38**, 337–342 (1990). https://doi.org/10.1346/CCMN.1990.0380401
83. Baloyi, J., Ntho, T., Moma, J.: Synthesis and application of pillared clay heterogeneous catalysts for wastewater treatment: A review. RSC Adv. **8**, 5197–5211 (2018). https://doi.org/10.1039/c7ra12924f
84. Schoonheydt, R.A., Pinnavaia, T., Lagaly, G., Gangas, N.: Pillared clays and pillared layered solids (Technical Report). Pure Appl. Chem. **71**, 2367–2371 (1999). https://doi.org/10.1351/pac199971122367

85. Li, F., Rosen, M.J.: Adsorption of gemini and conventional cationic surfactants onto montmorillonite and the removal of some pollutants by the clay. J. Colloid Interface Sci. **224**, 265–271 (2000). https://doi.org/10.1006/jcis.2000.6721
86. Schoonheydt, R.A., Jacobs, K.Y.: Clays: From two to three dimensions. In: van Bekkum, H., Flanigen, E.M., Jacobs, P.A., Jansen, J.C. (Eds.). Stud. Surf. Sci. Catal. Elsevier Science B.V., pp. 299–343 (2001). https://doi.org/10.1016/s0167-2991(01)80249-4
87. Ding, Z., Kloprogge, J.T., Frost, R.L., Lu, G.Q., Zhu, H.Y.: Porous clays and pillared clays-based catalysts. Part 2: A review of the catalytic and molecular sieve applications. J. Porous Mater. **8**, 273–293 (2001). https://doi.org/10.1023/A:1013113030912
88. Lin, S., Juang, R.: Heavy metal removal from water by sorption using surfactant-modified montmorillonite. J. Hazard. Mater. **92**, 315–326 (2002)
89. dos Santos, A., Viante, M.F., Pochapski, D.J., Downs, A.J., Almeida, C.A.P.: Enhanced removal of p-nitrophenol from aqueous media by montmorillonite clay modified with a cationic surfactant. J. Hazard. Mater. **355**, 136–144 (2018). https://doi.org/10.1016/j.jhazmat.2018.02.041
90. Speridião, D.D.C.A., dos Santos, O.A.A., de Almeida Neto, A.F., Vieira, M.G.A.: Characterization of spectrogel organoclay used to adsorption of petroleum derivatives. Mater. Sci. Forum. 798–799, 558–563 (2014). https://doi.org/10.4028/www.scientific.net/MSF.798-799.558
91. Stofela, S.K.F., de Almeida Neto, A.F., Gimenes, M.L., Vieira, M.G.A.: Adsorption of toluene into commercial organoclay in liquid phase: Kinetics, equilibrium and thermodynamics. Can. J. Chem. Eng. **93,** 998–1008 (2015). https://doi.org/10.1002/cjce.22174
92. Shah, K.H., Ghafoor, A., Fahad, M., Ali, S., Ahmad, H.: Natural ferruginous manganese ore as a potential low-cost adsorbent for Congo red dye removal from aqueous solution. Mater. Res. Express. **6**, 125515 (2019). https://doi.org/10.1088/2053-1591/ab56b8
93. Guégan, R., Giovanela, M., Warmont, F., Motelica-Heino, M.: Nonionic organoclay: A "Swiss Army knife" for the adsorption of organic micro-pollutants? J. Colloid Interface Sci. **437**, 71–79 (2015). https://doi.org/10.1016/j.jcis.2014.09.043
94. Wang, G., Wang, S., Sun, Z., Zheng, S., Xi, Y.: Structures of nonionic surfactant modified montmorillonites and their enhanced adsorption capacities towards a cationic organic dye. Appl. Clay Sci. **148**, 1–10 (2017). https://doi.org/10.1016/j.clay.2017.08.001
95. Shen, Y.H.: Preparations of organobentonite using nonionic surfactants. Chemosphere **44**, 989–995 (2001). https://doi.org/10.1016/S0045-6535(00)00564-6
96. Kamal, M.S.: A Review of Gemini Surfactants: Potential Application in Enhanced Oil Recovery. J. Surfactants Deterg. **19**, 223–236 (2016). https://doi.org/10.1007/s11743-015-1776-5
97. Shakil Hussain, S.M., Kamal, M.S., Murtaza, M.: Synthesis of novel ethoxylated quaternary ammonium gemini surfactants for enhanced oil recovery application. Energies. **12**, 1731 (2019). https://doi.org/10.3390/en12091731
98. Jain, A., Balasubramanian, R., Srinivasan, M.P.: Hydrothermal conversion of biomass waste to activated carbon with high porosity: A review. Chem. Eng. J. **283**, 789–805 (2016). https://doi.org/10.1016/j.cej.2015.08.014
99. Auta, M., Hameed, B.H.: Modified mesoporous clay adsorbent for adsorption isotherm and kinetics of methylene blue. Chem. Eng. J. **198–199**, 219–227 (2012). https://doi.org/10.1016/j.cej.2012.05.075
100. Unuabonah, E.I., Olu-Owolabi, B.I., Fasuyi, E.I., Adebowale, K.O.: Modeling of fixed-bed column studies for the adsorption of cadmium onto novel polymer-clay composite adsorbent. J. Hazard. Mater. **179**, 415–423 (2010). https://doi.org/10.1016/j.jhazmat.2010.03.020
101. Overesch, M., Rinklebe, J., Broll, G., Neue, H.U.: Metals and arsenic in soils and corresponding vegetation at Central Elbe river floodplains (Germany). Environ. Pollut. **145**, 800–812 (2007). https://doi.org/10.1016/j.envpol.2006.05.016
102. Han, H., Rafiq, M.K., Zhou, T., Xu, R., Mašek, O., Li, X.: A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants. J. Hazard. Mater. **369**, 780–796 (2019). https://doi.org/10.1016/j.jhazmat.2019.02.003

103. liang Liao, Z., Chen, H., Rong Zhu, B., Zheng Li, H.: Combination of powdered activated carbon and powdered zeolite for enhancing ammonium removal in micro-polluted raw water. Chemosphere. **134**, 127–132 (2015). https://doi.org/10.1016/j.chemosphere.2015.03.088
104. Wang, W., Tian, G., Zhang, Z., Wang, A.: A simple hydrothermal approach to modify palygorskite for high-efficient adsorption of Methylene blue and Cu(II) ions. Chem. Eng. J. **265**, 228–238 (2015). https://doi.org/10.1016/j.cej.2014.11.135
105. Ruiz-Hitzky, E., Van Meerbeek, A.: Clay mineral- and organoclay-polymer nanocomposite. In: Bergaya, F., Theng, B.K.G., Lagaly, G., (Eds.). Handb. Clay Sci., Elsevier Ltd., pp. 583–621 (2006). https://doi.org/10.1016/S1572-4352(05)01018-4
106. Yao, Y., Gao, B., Fang, J., Zhang, M., Chen, H., Zhou, Y., Creamer, A.E., Sun, Y., Yang, L.: Characterization and environmental applications of clay-biochar composites. Chem. Eng. J. **242**, 136–143 (2014). https://doi.org/10.1016/j.cej.2013.12.062
107. Belhouchat, N., Zaghouane-Boudiaf, H., Viseras, C.: Removal of anionic and cationic dyes from aqueous solution with activated organo-bentonite/sodium alginate encapsulated beads. Appl. Clay Sci. **135**, 9–15 (2017). https://doi.org/10.1016/j.clay.2016.08.031
108. Kumar, A.S.K., Kalidhasan, S., Rajesh, V., Rajesh, N.: Application of Cellulose-Clay Composite Biosorbent toward the Effective Adsorption and Removal of Chromium from Industrial Wastewater. Ind. Eng. Chem. Res. **51**, 58–69 (2012)
109. Barreca, S., Orecchio, S., Pace, A.: The effect of montmorillonite clay in alginate gel beads for polychlorinated biphenyl adsorption: Isothermal and kinetic studies. Appl. Clay Sci. **99**, 220–228 (2014). https://doi.org/10.1016/j.clay.2014.06.037
110. Shaban, M., Abukhadra, M.R., Shahien, M.G., Ibrahim, S.S.: Novel bentonite/zeolite-NaP composite efficiently removes methylene blue and Congo red dyes. Environ. Chem. Lett. **16**, 275–280 (2018). https://doi.org/10.1007/s10311-017-0658-7
111. Liang, G., Wang, Z., Yang, X., Qin, T., Xie, X., Zhao, J., Li, S.: Efficient removal of oxytetracycline from aqueous solution using magnetic montmorillonite-biochar composite prepared by one step pyrolysis. Sci. Total Environ. **695**, 133800 (2019). https://doi.org/10.1016/j.scitotenv.2019.133800
112. Li, Z., Cui, X., Ma, J., Chen, W., Gao, W., Li, R.: Preparation of granular X-type zeolite/activated carbon composite from elutrilithe by adding pitch and solid SiO2. Mater. Chem. Phys. **147**, 1003–1008 (2014). https://doi.org/10.1016/j.matchemphys.2014.06.051
113. Ma, J., Tan, J., Du, X., Li, R.: Effects of preparation parameters on the textural features of a granular zeolite/activated carbon composite material synthesized from elutrilithe and pitch. Microporous Mesoporous Mater. **132**, 458–463 (2010). https://doi.org/10.1016/j.micromeso.2010.03.027
114. Khanday, W.A., Marrakchi, F., Asif, M., Hameed, B.H.: Mesoporous zeolite–activated carbon composite from oil palm ash as an effective adsorbent for methylene blue. J. Taiwan Inst. Chem. Eng. **70**, 32–41 (2017). https://doi.org/10.1016/j.jtice.2016.10.029
115. Halim, A.A., Aziz, H.A., Johari, M.A.M., Ariffin, K.S.: Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment. Desalination **262**, 31–35 (2010). https://doi.org/10.1016/j.desal.2010.05.036
116. Mian, M.M., Liu, G.: Activation of peroxymonosulfate by chemically modified sludge biochar for the removal of organic pollutants: Understanding the role of active sites and mechanism. Chem. Eng. J. **392**, 123681 (2020). https://doi.org/10.1016/j.cej.2019.123681
117. Li, F., Cao, X., Zhao, L., Wang, J., Ding, Z.: Effects of mineral additives on biochar formation: Carbon retention, stability, and properties. Environ. Sci. Technol. **48**, 11211–11217 (2014). https://doi.org/10.1021/es501885n
118. Ashiq, A., Adassooriya, N.M., Sarkar, B., Rajapaksha, A.U., Ok, Y.S., Vithanage, M.: Municipal solid waste biochar-bentonite composite for the removal of antibiotic ciprofloxacin from aqueous media. J. Environ. Manage. **236**, 428–435 (2019). https://doi.org/10.1016/j.jenvman.2019.02.006
119. Chaukura, N., Chiworeso, R., Gwenzi, W., Motsa, M.M., Munzeiwa, W., Moyo, W., Chikurunhe, I., Nkambule, T.T.I.: A new generation low-cost biochar-clay composite ‘biscuit’ ceramic filter for point-of-use water treatment. Appl. Clay Sci. **185**, 105409 (2020). https://doi.org/10.1016/j.clay.2019.105409

120. Yang, F., Zhao, L., Gao, B., Xu, X., Cao, X.: The Interfacial Behavior between Biochar and Soil Minerals and Its Effect on Biochar Stability. Environ. Sci. Technol. **50**, 2264–2271 (2016). https://doi.org/10.1021/acs.est.5b03656
121. Ashiq, A., Sarkar, B., Adassooriya, N., Walpita, J., Rajapaksha, A.U., Ok, Y.S., Vithanage, M.: Sorption process of municipal solid waste biochar-montmorillonite composite for ciprofloxacin removal in aqueous media. Chemosphere **236**, 124384 (2019). https://doi.org/10.1016/j.chemosphere.2019.124384
122. Pan, X., Gu, Z., Chen, W., Li, Q.: Preparation of biochar and biochar composites and their application in a Fenton-like process for wastewater decontamination: A review. Sci. Total Environ. **754**, 142104 (2021). https://doi.org/10.1016/j.scitotenv.2020.142104
123. Zhang, M., Gao, B., Yao, Y., Inyang, M.: Phosphate removal ability of biochar/MgAl-LDH ultra-fine composites prepared by liquid-phase deposition. Chemosphere **92**, 1042–1047 (2013). https://doi.org/10.1016/j.chemosphere.2013.02.050
124. Zhang, M., Yao, Q., Guan, W., Lu, C., Lin, J.M.: Layered double hydroxide-supported carbon dots as an efficient heterogeneous Fenton-like catalyst for generation of hydroxyl radicals. J. Phys. Chem. C. **118**, 10441–10447 (2014). https://doi.org/10.1021/jp5012268
125. Wan, S., Wang, S., Li, Y., Gao, B.: Functionalizing biochar with Mg–Al and Mg–Fe layered double hydroxides for removal of phosphate from aqueous solutions. J. Ind. Eng. Chem. **47**, 246–253 (2016). https://doi.org/10.1016/j.jiec.2016.11.039
126. Jung, K.W., Hwang, M.J., Jeong, T.U., Ahn, K.H.: A novel approach for preparation of modified-biochar derived from marine macroalgae: Dual purpose electro-modification for improvement of surface area and metal impregnation. Bioresour. Technol. **191**, 342–345 (2015). https://doi.org/10.1016/j.biortech.2015.05.052
127. Tan, X., Liu, Y., Gu, Y., Liu, S., Zeng, G., Cai, X., Hu, X., Wang, H., Liu, S., Jiang, L.: Biochar pyrolyzed from MgAl-layered double hydroxides pre-coated ramie biomass (Boehmeria nivea (L.) Gaud.): Characterization and application for crystal violet removal. J. Environ. Manage. **184**, 85–93 (2016). https://doi.org/10.1016/j.jenvman.2016.08.070
128. Chen, B., Evans, J.R.G., Greenwell, H.C., Boulet, P., Coveney, P.V., Bowden, A.A., Whiting, A.: A critical appraisal of polymer–clay nanocomposites. Chem. Soc. Rev. **37**, 568–594 (2008). https://doi.org/10.1039/b702653f
129. Rusmin, R., Sarkar, B., Liu, Y., McClure, S., Naidu, R.: Structural evolution of chitosan-palygorskite composites and removal of aqueous lead by composite beads. Appl. Surf. Sci. **353**, 363–375 (2015). https://doi.org/10.1016/j.apsusc.2015.06.124
130. Xie, F., Pollet, E., Halley, P.J., Avérous, L.: Starch-based nano-biocomposites. Prog. Polym. Sci. **38**, 1590–1628 (2013). https://doi.org/10.1016/j.progpolymsci.2013.05.002
131. Pavlidou, S., Papaspyrides, C.D.: A review on polymer-layered silicate nanocomposites. Prog. Polym. Sci. **33**, 1119–1198 (2008). https://doi.org/10.1016/j.progpolymsci.2008.07.008
132. Hernández-Hernández, K.A., Illescas, J., del Díaz-Nava, M.C., Martínez-Gallegos, S., Muro-Urista, C., Ortega-Aguilar, R.E., Rodríguez-Alba, E., Rivera, E.: Preparation of nanocomposites for the removal of phenolic compounds from aqueous solutions. Appl. Clay Sci. **157**, 212–217 (2018). https://doi.org/10.1016/j.clay.2018.01.020
133. Wang, W., Tian, G., Zong, L., Wang, Q., Zhou, Y., Wang, A.: Mesoporous hybrid Zn-silicate derived from red palygorskite clay as a high-efficient adsorbent for antibiotics. Microporous Mesoporous Mater. **234**, 317–325 (2016). https://doi.org/10.1016/j.micromeso.2016.07.029
134. Cheng, W.P., Gao, W., Cui, X., Ma, J.H., Li, R.F.: Phenol adsorption equilibrium and kinetics on zeolite X/activated carbon composite. J. Taiwan Inst. Chem. Eng. **62**, 192–198 (2016). https://doi.org/10.1016/j.jtice.2016.02.004
135. Chattopadhyaya, M.C., Gautam, R.K.: Advanced nanomaterials for wastewater remediation, 1st edn. CRC Press, (2017)
136. Kim, T.-H., Lee, W.-J., Lee, J.-Y., Paek, S.-M., Oh, J.-M.: Isomorphous substitution of divalent metal ions in layered double hydroxides through a soft chemical hydrothermal reaction. Dalt. Trans. **43**, 10430 (2014). https://doi.org/10.1039/c4dt00373j
137. Xu, M., Wei, M.: Layered double hydroxide-based catalysts: recent advances in preparation, structure, and applications. Adv. Funct. Mater. **28**, 1–20 (2018). https://doi.org/10.1002/adfm.201802943

138. Gautam, R.K., Singh, A.K., Tiwari, I.: Nanoscale layered double hydroxide modified hybrid nanomaterials for wastewater treatment: A review. J. Mol. Liq. **350**, 118505 (2022). https://doi.org/10.1016/j.molliq.2022.118505
139. Rojas, R.: Copper, lead and cadmium removal by Ca Al layered double hydroxides. Appl. Clay Sci. **87**, 254–259 (2014). https://doi.org/10.1016/j.clay.2013.11.015
140. González, M.A., Pavlovic, I., Barriga, C.: Cu(II), Pb(II) and Cd(II) sorption on different layered double hydroxides. A kinetic and thermodynamic study and competing factors. Chem. Eng. J. **269**, 221–228 (2015). https://doi.org/10.1016/j.cej.2015.01.094
141. Yang, F., Sun, S., Chen, X., Chang, Y., Zha, F., Lei, Z.: Mg–Al layered double hydroxides modified clay adsorbents for efficient removal of Pb 2+, Cu 2+ and Ni 2+ from water. Appl. Clay Sci. **123**, 134–140 (2016). https://doi.org/10.1016/j.clay.2016.01.026
142. Chen, L., Tu, Q., Yang, X., Hu, X., Sun, X., Li, H.: MgAl layered double hydroxides intercalated with EDTA: Cu(II) recovery and mechanism. Chemistry Select **5**, 11299–11304 (2020). https://doi.org/10.1002/slct.202003011
143. Fdez-Sanromán, A., Pazos, M., Rosales, E., Sanromán, M.A.: Unravelling the environmental application of biochar as low-cost biosorbent: A review. Appl. Sci. **10**, 7810 (2020). https://doi.org/10.3390/app10217810
144. Li, J., Yan, L., Yang, Y., Zhang, X., Zhu, R., Yu, H.: Insight into the adsorption mechanisms of aqueous hexavalent chromium by EDTA intercalated layered double hydroxides: XRD, FTIR, XPS, and zeta potential studies. New J. Chem. **43**, 15915–15923 (2019). https://doi.org/10.1039/C9NJ03479J
145. Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S.: Biochar as a sorbent for contaminant management in soil and water: A review. Chemosphere **99**, 19–33 (2014). https://doi.org/10.1016/j.chemosphere.2013.10.071
146. Zhang, Y., Wang, S., Feng, D., Gao, J., Dong, L., Zhao, Y., Sun, S., Huang, Y., Qin, Y.: Functional Biochar Synergistic Solid/Liquid-Phase CO 2 Capture: A Review. Energy Fuels **36**, 2945–2970 (2022). https://doi.org/10.1021/acs.energyfuels.1c04372
147. Gao, F., Xu, Z., Dai, Y.: Removal of tetracycline from wastewater using magnetic biochar: A comparative study of performance based on the preparation method. Environ. Technol. Innov. **24**, 101916 (2021). https://doi.org/10.1016/j.eti.2021.101916
148. Kapoor, T.R., Treichel, H., Shah, M.P.: Biochar and its Application in Bioremediation, Springer Nature Singapore. Singapore (2021). https://doi.org/10.1007/978-981-16-4059-9
149. Wang, H., Xu, J., Sheng, L.: Preparation of straw biochar and application of constructed wetland in China: A review. J. Clean. Prod. **273**, 123131 (2020). https://doi.org/10.1016/j.jclepro.2020.123131
150. Zhu, L., Yang, H., Zhao, Y., Kang, K., Liu, Y., He, P., Wu, Z., Wei, Z.: Biochar combined with montmorillonite amendments increase bioavailable organic nitrogen and reduce nitrogen loss during composting. Bioresour. Technol. **294**, 122224 (2019). https://doi.org/10.1016/j.biortech.2019.122224
151. Tang, J., Zong, L., Mu, B., Zhu, Y., Wang, A.: Preparation and cyclic utilization assessment of palygorskite/carbon composites for sustainable efficient removal of methyl violet. Appl. Clay Sci. **161**, 317–325 (2018). https://doi.org/10.1016/j.clay.2018.04.039
152. Rallet, D., Paltahe, A., Tsamo, C., Loura, B.: Synthesis of clay-biochar composite for glyphosate removal from aqueous solution. Heliyon. **8**, e09112 (2022). https://doi.org/10.1016/j.heliyon.2022.e09112
153. Gao, L., Goldfarb, J.L.: Characterization and adsorption applications of composite biochars of clay minerals and biomass. Environ. Sci. Pollut. Res. **28**, 44277–44287 (2021). https://doi.org/10.1007/s11356-021-13858-x
154. dos Santos Lins, P.V., Henrique, D.C., Ide, A.H., de Paiva e Silva Zanta, C.L., Meili, L.: Evaluation of caffeine adsorption by MgAl-LDH/biochar composite, Environ. Sci. Pollut. Res. **26**, 31804–31811 (2019). https://doi.org/10.1007/s11356-019-06288-3
155. Raimundo, C.M.: Contaminantes emergentes em água tratada e seus mananciais: sazonalidade. remoção e atividade estrogênica, 203(2011)

156. Geissen, V., Mol, H., Klumpp, E., Umlauf, G., Nadal, M., van der Ploeg, M., van de Zee, S.E.A.TM., Ritsema, C.J.: Emerging pollutants in the environment: A challenge for water resource management. Int. Soil Water Conserv. Res. **3**, 57–65 (2015). https://doi.org/10.1016/j.iswcr.2015.03.002
157. Santos, L.C., da Silva, A.F., dos Santos Lins, P.V., da Silva Duarte, J.L., Ide, A.H., Meili, L.: Mg-Fe layered double hydroxide with chloride intercalated: synthesis, characterization and application for efficient nitrate removal. Environ. Sci. Pollut. Res. **27**, 5890–5900 (2020). https://doi.org/10.1007/s11356-019-07364-4
158. Meili, L., Lins, P.V.S., Costa, M.T., Almeida, R.L., Abud, A.K.S., Soletti, J.I., Dotto, G.L., Tanabe, E.H., Sellaoui, L., Carvalho, S.H.V., Erto, A.: Adsorption of methylene blue on agroindustrial wastes: Experimental investigation and phenomenological modelling. Prog. Biophys. Mol. Biol. **141**, 60–71 (2019). https://doi.org/10.1016/j.pbiomolbio.2018.07.011
159. Viglašová, E., Galamboš, M., Danková, Z., Krivosudský, L., Lengauer, C.L., Hood-Nowotny, R., Soja, G., Rompel, A., Matík, M., Briančin, J.: Production, characterization and adsorption studies of bamboo-based biochar/montmorillonite composite for nitrate removal. Waste Manag. **79**, 385–394 (2018). https://doi.org/10.1016/j.wasman.2018.08.005
160. Song, J., Zhang, S., Li, G., Du, Q., Yang, F.: Preparation of montmorillonite modified biochar with various temperatures and their mechanism for Zn ion removal. J. Hazard. Mater. **391**, 121692 (2020). https://doi.org/10.1016/j.jhazmat.2019.121692
161. Xue, L., Gao, B., Wan, Y., Fang, J., Wang, S., Li, Y., Muñoz-Carpena, R., Yang, L.: High efficiency and selectivity of MgFe-LDH modified wheat-straw biochar in the removal of nitrate from aqueous solutions. J. Taiwan Inst. Chem. Eng. **63**, 312–317 (2016). https://doi.org/10.1016/j.jtice.2016.03.021
162. Yu, J., Zhu, Z.: Mg—Fe layered double hydroxide assembled on biochar derived from rice husk ash : facile synthesis and application in efficient removal of heavy metals+有O的XPS, 24293–24304 (2018)
163. Jia, Y., Zhang, Y., Fu, J., Yuan, L., Li, Z., Liu, C., Zhao, D., Wang, X.: A novel magnetic biochar/MgFe-layered double hydroxides composite removing Pb 2+ from aqueous solution: Isotherms, kinetics and thermodynamics. Colloids Surfaces A Physicochem. Eng. Asp. **567**, 278–287 (2019). https://doi.org/10.1016/j.colsurfa.2019.01.064
164. Cui, Q., Jiao, G., Zheng, J., Wang, T., Wu, G., Li, G.: Synthesis of a novel magnetic: Caragana korshinskii biochar/Mg-Al layered double hydroxide composite and its strong adsorption of phosphate in aqueous solutions. RSC Adv. **9**, 18641–18651 (2019). https://doi.org/10.1039/c9ra02052g
165. He, H., Zhang, N., Chen, N., Lei, Z., Shimizu, K., Zhang, Z.: Efficient phosphate removal from wastewater by MgAl-LDHs modified hydrochar derived from tobacco stalk. Bioresour. Technol. Reports. **8**, 100348 (2019). https://doi.org/10.1016/j.biteb.2019.100348
166. Jiang, Y.H., Li, A.Y., Deng, H., Ye, C.H., Li, Y.: Phosphate adsorption from wastewater using ZnAl-LDO-loaded modified banana straw biochar. Environ. Sci. Pollut. Res. **26**, 18343–18353 (2019). https://doi.org/10.1007/s11356-019-05183-1
167. Lee, S.Y., Choi, J.W., Song, K.G., Choi, K., Lee, Y.J., Jung, K.W.: Adsorption and mechanistic study for phosphate removal by rice husk-derived biochar functionalized with Mg/Al-calcined layered double hydroxides via co-pyrolysis. Compos. Part B Eng. **176**, 107209 (2019). https://doi.org/10.1016/j.compositesb.2019.107209
168. Huang, D., Liu, C., Zhang, C., Deng, R., Wang, R., Xue, W., Luo, H., Zeng, G., Zhang, Q., Guo, X.: Cr(VI) removal from aqueous solution using biochar modified with Mg/Al-layered double hydroxide intercalated with ethylenediaminetetraacetic acid. Bioresour. Technol. **276**, 127–132 (2019). https://doi.org/10.1016/j.biortech.2018.12.114
169. Lins, P.V.S., Henrique, D.C., Ide, A.H., da silva Duarte, J.L., Dotto, G.L., Yazidi, A., Sellaoui, L., Erto, A., de P. e. S. Zanta, C.L., Meili, L.: Adsorption of a non-steroidal anti-inflammatory drug onto MgAl/LDH-activated carbon composite—Experimental investigation and statistical physics modeling, Colloids Surfaces A Physicochem. Eng. Asp. **586**, 124217(2020). https://doi.org/10.1016/j.colsurfa.2019.124217

170. Fang, Q., Ye, S., Yang, H., Yang, K., Zhou, J., Gao, Y., Lin, Q., Tan, X., Yang, Z.: Application of layered double hydroxide-biochar composites in wastewater treatment: Recent trends, modification strategies, and outlook. J. Hazard. Mater. **420**, 126569 (2021). https://doi.org/10.1016/j.jhazmat.2021.126569
171. Zubair, M., Ihsanullah, I., Aziz, H.A., Ahmad, M.A. and Al-Harthi, M.A.: Sustainable wastewater treatment by biochar/layered double hydroxide composites: Progress, challenges, and outlook. Bioresour. Technol. **319**, 124128(2021). https://doi.org/10.1016/j.biortech.2020.124128
172. Das, R., Panda, S.N.: Preparation and applications of biochar based nanocomposite: A review. J. Anal. Appl. Pyrolysis. **167**, 105691 (2022). https://doi.org/10.1016/j.jaap.2022.105691
173. Gabriel, R., De Carvalho, S.H., da Silva Duarte, J.L., Oliveira, L.M., Giannakoudakis, D.A., Triantafyllidis, K.S., Soletti, J.I., Meili, L.: Mixed metal oxides derived from layered double hydroxide as catalysts for biodiesel production. Appl. Catal. A Gen. **630**, (2022). https://doi.org/10.1016/j.apcata.2021.118470

Clay-Biochar Composites: Emerging Applications in Soil

Muhammad Imran Rafique, Jahangir Ahmad, Muhammad Usama, Munir Ahmad, Hamed A. Al-Swadi, Abdullah S. F. Al-Farraj, and Mohammad I. Al-Wabel

Abstract Clay-biochar composites have widely been employed to improve soil quality, fertility, crop productivity, nutrient retention, carbon sequestration, as well as to immobilize organic and inorganic pollutants, and reduce greenhouse gases emission. Several natural clay minerals are smaller in size with poor flow-ability and cannot be used exclusively. Therefore, combining clays with biochar could combine the benefits of both materials and exhibited superior performance when applied as soil amendments. Therefore, the potential applications and mechanistic insights of clay-biochar composites in soil are reviewed and discussed in this chapter. Moreover, the environmental and agricultural performance of different clay-biochar composites, factors affecting the properties and performance of clay-biochar composites, and significance of these composites in mitigating climate change are discussed. Furthermore, future research challenges in synthesis of clay-biochar composites and their application in soil are proposed.

Keywords Climate change · Food security · Environmental pollution · Adsorption · Nutrient retention

1 Introduction

The rapid rate of urbanization and industrialization as a result of various anthropogenic ventures has emerged as a source of environmental pollution [1]. As a consequence of these anthropogenic activities, several kinds of waste are discharged into

---

M. I. Rafique · J. Ahmad · M. Usama · M. Ahmad · H. A. Al-Swadi · A. S. F. Al-Farraj · M. I. Al-Wabel (✉)
Soil Sciences Department, College of Food and Agricultural Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia
e-mail: malwabel@ksu.edu.sa

H. A. Al-Swadi
Faculty of Agriculture, Food and Environment, Department of Soil, Water and Environment, Sana'a University, Sana'a, Yemen

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_7

water bodies and terrestrial environment, which ultimately cause serious environmental deterioration. Such kind of waste includes number of organic and inorganic pollutants, soluble salts, partially decomposed farm yard waste, and several kind of pharmaceutical wastes. Among these pollutants, several pollutants are classified for their tenacious nature and severe toxicity such as some carbon based pollutants and heavy metals [2]. Along with surface soil contamination, these pollutants deteriorate ground water resources due to leaching and lateral movement which poses serious threats to plant growth, microbial activity, and human health as well [3]. Hence, it is important to overcome such kind of environmental pollution and restoration of terrestrial and aquatic resources by utilization of some feasible strategies and practical techniques. A number of techniques have been tried earlier for riddance of these pollutants including precipitation, adsorption, bio-sorption, ion exchange, filtration, coagulation, and cementation/ stabilization. Due to its feasibility, easy to practice and being economical, adsorption is widely accepted technique among them [4].

Many adsorbents have been utilized earlier for adsorption of such pollutants and among them clay minerals are easily available and viable adsorbent. Clays are hydrous aluminosilicate minerals composed of a mixture of fine-grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonates, and metal oxides [5]. Clays have the potential to act as natural scavengers for heavy metals and other pollutants in polluted soil and water systems [6]. Clay minerals have a quite high surface area [7] along with easy accessibility, non-toxic and have lamellar structure [8]. Due to surface negative charge, clay minerals have tendency for surface sorption and exchange of cationic inorganic and organic pollutants [9]. These properties of clay minerals make it suitable adsorbent for heavy metals immobilization and removal of several other organic pollutants as well [10]. Though being a good adsorbent of several pollutants, clay minerals have some surface characteristics which constraint their adsorption efficiency. Combination of clay minerals with organic materials such as compost, biosolids, chicken waste, farmyard manure could be suitable strategy to improve their surface characteristics and adsorption efficiency [11].

Biochar is one of the organic adsorbents which can be combined with clay minerals to make clay-biochar composite. Biochar is solid by product of controlled combustion of organic wastes and possess high surface area, porous structure, plenty of surface functional groups, high cation exchange capacity, and excellent adsorption capacity for several kind of pollutants [12, 13]. Clay-biochar composite supports and reinforces each other sorptive characteristics and improves adsorption efficiency. A composite of bark chip biochar with montmorillonite effectively immobilizes Cu, Zn, and Pb in metal contaminated soil by ion exchange mechanism [14]. Bamboo-derived biochar acts as a slow-released fertilizer for NH_4^+ when co-pyrolyzed with clay mineral montmorillonite [15, 16]. Wang et al. [17] reported that biochar and Si-rich montmorillonite composite effectively remediates AS contaminated soil. Struvite (NH_4MgPO_4) is a nutrient-rich mineral that has been commonly used as a fertilizer. Co-precipitation of struvite with biochar could enhance the slow-release behavior of composite which ultimately favors soil fertility and metal immobilization [18, 19, 20]. Mineral additives can also reduce the potential toxicity of biochar produced from waste materials, making it more useful material for soil application [21]. Earlier studies also reported promising results in enhancing soil carbon fraction and carbon sequestration by soil application of various kind of clay-biochar composites [22, 23, 24]. Therefore, utilization of clay minerals by making their composites with other organic materials such as biochar might be helpful in improving their surface characteristics and adsorption efficiency and also make them suitable material for various soil application.

2 Applications of Clay Minerals and Biochar to Solve the Major Soil Problems

Clay minerals have been used in the past in multiple ways such as catalyst, coagulants, colloid stabilizers, chemicals support, coating material, cosmetics, sorbents, pottery, drilling, filling, and construction material. In the modern era, natural clay minerals are being used worldwide as efficient adsorbents. Clay minerals have a very important role in the agriculture sectors and have been used in the past for several purposes [25]. From the last few decades, clay is being used to remove heavy metals and several other pollutants such as dyes [26] and fluorides [27]. These clays contain a huge number of pores with large surface area which enable them as suitable substrate for ion exchange and adsorption. Additionally, being easily available, non-toxic, economical, and ecofriendly materials, clay minerals have wide scale industrial and environmental applications. Montmorillonite, bentonite, and attapulgite minerals are commonly used to mitigate heavy metals toxicity and decrease their mobility by surface sorption mechanism [28]. In another study, Zhang et al. [29] found 88.7% removal of Cu from Cu contaminated soil after application of attapulgite clay deposits for 2 months. Zotiadis and Argyraki [30] conducted a field experiment using attapulgite clay deposits for the removal of heavy metals from metal contaminated soil, and they reported the excellent adsorption capacity of attapulgite. Zhang et al. [28] found higher soil pH and 24.7% decline in Cu concentration in Cu contaminated soil by addition of montmorillonite. In a field study to observe influence of combined application of Ca-bentonite, Na-bentonite, and zeolite, Usman et al. [31] found up to 57% decrease in heavy metal concentration. Cd was removed from the brown rice, during field and pot experiment using sepiolite, and it was noted that with increasing pH and dose rate, adsorption was increased [32]. Although clay minerals have been endorsed for having good adsorptive characteristics, but their adsorption capacity is mediocre occasionally which could be due to their layer structure and surface ions. Biochar is an emerging technology in the recent times, and it is hypothesized that by combining both adsorbents (clay and biochar) will reinforce their sorptive characteristics.

Biochar, which is produced by the thermal combustion of organic waste under a controlled supply of oxygen, has ample potential to increase soil and water ecosystem quality. High cation exchange capacity, mechanical strength, adsorption capacity, organic carbon content, long half-life, nutrient, and water holding capacity make biochar a pragmatic material for soil remediation [33]. Biochar is equipped with porous surface, net negative surface charge, and bundle of functional groups, which make it an efficient adsorbent for long range of organic and inorganic pollutants. In addition to its application for soil remediation, biochar has been also applied to improve soil quality and productivity by increasing essential nutrient and water holding capacity of soil [34]. Toxic metals/metalloids and organic contaminants can be efficiently adsorbed by the biochar [35]. As a result, these contaminants become unavailable for plants, humans, animal, and environment. Hence, biochar could be used effectively as a remediation tool to decontaminate the soil.

3 Constraints in the Application of Clay and Biochar

Clay minerals are non-expensive, easy to handle, effective, and environment friendly, but there are some drawbacks which need to be solved. There are some factors that influence the properties of clays that include exchangeable cations, soluble salts, and texture of the clays. Cations present in the octahedral and tetrahedral sheets of minerals causes the charge deficit and less efficiency toward ions sorption. Sometime a mixture of cations is found on the surface and sheets of the naturally deposited clays which makes it impossible to use the clays for certain purposes. Cations found in the interlayer spaces, helps to make the physiochemical characteristics unique for certain applications. Texture and structure of the clays have a great effect on the adsorption capacities of the clays. Therefore, before selecting and using the clays, the mentioned factors should be considered. To increase the surface area, permeability, and adsorption capacity of the clay minerals, they need to be modified. There are different modification techniques including ion exchange, inorganic and organic complexes/binding, pillaring with poly cations acid treatments, inter- and intra-particle polymerization, ultrasonication, and physical treatments [36, 37]. Montmorillonite is a 2:1 clay type, hydrophilic in nature which makes it unable for polymer matrices. Some of the clays show a less reactivity, low adsorption capacity, and low surface area when they are in natural forms for example kaolin [38]. It was also reported that when bentonite was used to remove dye, the negative charge on the surface caused the repulsion of the dye and showed less adsorption [39, 40]. Clay minerals are not efficient adsorbent all the time, sometime they don't perform well. For example, montmorillonite has net negative charge and sometimes it adsorbed cationic dyes which include methylene blue, rhodamine B, crystal violet [41]. To minimize the addressed problems, clay minerals could be combined with biochar to make the composites which could reinforce the adsorption capacity of both adsorbents.

Although, clay and biochar are being used to treat the soil problems; they are being applied both individually and in the form of composites. However, there are some kinds of limitations that need to be overcome before their applications to the soil. Clay and biochar, no doubt are easy to prepare, handle, environment friendly, and cost effective, but while preparing their composites some kinds of problems have been noted such as the need of some expensive chemicals to be added and release of chemicals and by products to the environment [42]. Its very challenging to deal with organic compounds and plausible research work has been conducted to find best suited organic compound, which needs further interpretation and analytical trials in variable environmental conditions. Moreover, ammonium surfactants have health effects to the researchers. Ammonium salts may accumulate in the environment when organic compounds are used [42].

4 Application of Clay-Biochar Composites in Soil

Clay minerals, which are recognized for their excellent adsorptive characteristics, exclusive layer structure, surface chemistry, high ion exchange capacity, and wide surface area have broad industrial, agricultural, and petroleum application. Such revered surface and interlayer properties make them worthy and effective adsorbent for heavy metals, dyes, wastewater, and soil-based organic and inorganic pollutants [43]. Even though, excellent ion exchange capacity, broad specific surface area, sorptive properties, and interlayer chemistry allow broad environmental application of clay, in natural conditions, certain surface properties and presence of diverse cations on surface and in interlayers of clay minerals make their environmental application near impossible [37]. Generally, clay minerals are modified to enhance their surface properties, permeability, ion exchange capacity, to add desired surface and interlayer cations, and to improve adsorption ability. Clay minerals are modified by numerous ways such as addition of inorganic/organic complexes of cations and anions, binding of specific cation and anions specifically on edges, acid modification, clay-metal hydroxide complexes, inter- and intra-particle polymerization, and physical treatment with some organic materials including compost, chicken manure, activated carbon, and carbon nanotubes [44, 36, 37]. Modification of clay minerals with organic materials geneses intercalation of large organic molecules in layers of clay, which leads to expansion of clay minerals and organic ions (cations and anions) addition. Such sort of clay mineral interlayer expansion and ions addition enhances surface charge and specific surface area, increases ion exchange capacity, and improves its sorptive characteristics. Biochar, which is pyrogenic carbonaceous organic material produced by controlled combustion of organic waste has received plausible attention as soil amendment and carbon fixer [45]. On its application as soil amendment, biochar improves soil quality, enhances crop productivity, soil nutrient and water holding capacity, mitigate greenhouse gases emission, and lastly carbon sequestration. Combination of clay with biochar generate clay-biochar composite which results in upgraded functionalities and improved environmental application of both materials. Biochar provides porous structure, which eventually host and sustenance distribution micro- and nano-particles of clay within carbonic matrix of biochar [46]. Generation of such kind of composite by using two low cost materials (biochar-clay) could be helpful in improving soil fertility, soil quality, removing various inorganic and organic pollutants, mitigating greenhouse gases emission, and finally carbon sequestration on its soil application.

4.1 Soil Fertility and Crop Production

Insight to sustainable consumption of esteemed soil resources, soil quality and productivity have emerged as widely accredited conception, undertaking soil restraints at varied dimensions and adapting management practices to ensure long-term sustained soil fertility and crop productivity. In general, due to over utilization and lacking management practices, globally soil faces a number of quality related concerns including poor soil structure, water holding capacity, nutrient loss by leaching, organic and inorganic contamination, poor activity, and lower population of soil microorganisms and faunal depletion [47]. Recent application of advanced biochar-clay composites worked very well in improving soil fertility and overall crop productivity by restoring and improving soil structure and texture, enhancing soil porosity and water holding capacity, replenishing soil with essential nutrients, halting nutrient loss by leaching, fixing, and completely immobilizing soil and water born organic and inorganic pollutants (Table 1). Combination of organo-clay minerals with biochar effectively improved soil structure and soil aggregation acting as cementing agent [48]. Chen et al. [15, 16] stated that a montmorillonite-biochar composite showed great potential in control releasing of NH_4^+ and PO_4^{3-}. The retention of NH_4^+ revealed high cation exchange capacity of montmorillonite, and PO_4^{3-} availability was linked to ionic bonding on cationic surface of biochar. In a nutshell, an ultimate clay-biochar composite for soil fertility possess abundant porous structures with higher ion exchange capacity; however, sorption of nutrients should be reversible for better uptake by plants.

4.2 Immobilization of Organic Pollutants

In comparison with inorganic contaminants, which are persistent in soil for longer period due to their slow leaching nature, organic pollutants such as herbicides and pharmaceutical waste are more persistent in soil with half-life of more than 100 years [2]. Extensive scientific work has been conducted on biochar to use it as an adsorbent for such inorganic and organic contaminants, since it has been endorsed as an economical, environment friendly, and efficient adsorbent against other existing adsorbents and remediation techniques which have high investment cost and poor efficiency against a range of adsorbents [53, 54, 55]. Additionally, treating biochar with a number of foreign materials such as metal/metal oxide impregnation, elemental coating, nutrient enrichment, polymerization, and clay-biochar composite to improve its surface properties, reinforce its potential in removing toxic organic and inorganic pollutants [56, 57]. Owing to its net negative surface charge,

Table 1 Soil application of various clay mineral-biochar composites

Clay mineral	Biochar feedstock	Preparation method	Soil application	Performance	Reference
Struvite	Wheat straw	Co-precipitation	Controlled release fertilizer	Continuous supply of P for over period of 2 months	Hu et al. [18]
Montmorillonite	Bamboo	Co-pyrolysis	Slow-release fertilizer	Controlled release of NH_4^+ (0.3–4.9%) within 1–4 days	Chen et al. [15, 16]
Attapulgite	Yak dung	Co-pyrolysis	To promote pasture growth	Higher soil productivity and 12.8% increase in pasture biomass	Rafiq et al. [49]
Natural clay	Yak dung	Co-pyrolysis	Grazing field application to enhance bluegrass production	A positive impact on yield and quality of bluegrass and soil properties	Rafiq et al. [49]
Bentonite	Cotton straw	Impregnation	Slow release of nutrients in soil	Around 72.6% release of P within 2 weeks	An et al. [50]
Struvite		Impregnation	As N, P fertilizer to improve soil nutrient availability	During period of 3 months N and P release was 10.62 and 6.84% cumulatively	Hu et al. [18]
Montmorillonite	Cotton stalks and cotton straw	Impregnation encapsulation	Biochar and biofilm composite toward P SRF in soil	The cumulative PO_4^{3-} release after 30 d was 76, 65, 60, and 53.5% for each type of composite	An et al. [51]
Bentonite	Cotton stalks	Encapsulation	Enhance nutrient retention and availability in soil	Below 80% release of N. P and K during period of 1 month	An et al. [52]

clay minerals are also recognized as good adsorbent of cationic inorganic pollutants such as heavy metals and organic pollutants including dyes and herbicides [9]. Clay-biochar composite proves very useful in removing organic toxins and also reinforces each other sorptive and surface properties to further improve their adsorption capacities. A number of previous studies reported that clay-biochar composites successfully removed higher amount of organic pollutants than biochar and clay alone (Table 2). Kim et al. [58] reported 61% and 72% removal efficiency of atenolol by employing biochar and biochar-kaolinite (BC-KLN) composite (1:5 ratio), respectively. Similarly, Zhang et al. [29] found 143% more adsorption of norfloxacin (NOR) by biochar-montmorillonite (BC-MMT) composites against biochar alone. Consequently, utilization of different kind of clay-biochar composites to remove organic pollutants from terrestrial and aqueous environment proves beneficial and effective.

4.3 Immobilization of Inorganic Pollutants

Biochar composites with various clay minerals aid in immobilization and removal of inorganic pollutants in terrestrial and aquatic environments in many ways. Former studies showed excellent potential of clay-biochar composites in mitigating and finally completely removing toxic effects of inorganic pollutants. In a research study, Wang et al. [17] found significance of biochar-palygorskite composite in removing arsenic (As) contents from a river stream, which were 1.20 mg L^{-1} and 0.20 mg L^{-1} overlaying in water stream after treating contaminated water with biochar alone and biochar-palygorskite composite, respectively. Arif et al. [65] found lowest mobility index of 0.350 for Cd in soil by application nano-clay and biochar composite, which was 0.518 by using walnut derived biochar alone. Rice straw biochar and montmorillonite composite absorbed 80% more nitrate from aquatic medium than treating same water with unmodified biochar [66]. Overall findings of many previous studies proved effective utilization of biochar for adsorption stabilization of inorganic pollutants from aquatic medium and soil, which can be further improved by biochar modification and producing clay-biochar composites (Table 3).

4.4 Mitigation of Climate Change

Recycling of organic feedstock in to some valuable product such as biochar, is a plausible strategy in lessening harmful effects of climate change. Biochar application to offset global warming has been advocated previously with an anticipated potential to lessen anthropogenic flux of CO_2–C by 12% in equivalence with greenhouse gases emission (GHG) [70, 71]. Earlier, many studies endorsed virgin biochar potential in mitigating GHG emission and ultimately lowering global warming; however, recent research work showed utilization of biochar composites further improved its efficacy in alleviating GHG emission and overall climate change [72, 70]. Evidences showed co-pyrolysis of feedstock with clay mineral enhanced biochar aromaticity, soil stability, and long-term soil carbon storage [73, 10]. The stable bond between Si–C in Si-biochar composite indicated higher carbon stability of biochar on its soil application [74]. GHG release in soil amended with biochar composite is regulated by both type of biochar composite and soil physical properties with more effective mitigation of GHG emission in course textured soil [10] (Table 4).

Table 2 Potential application of clay-biochar composites in removing organic contaminant

Contaminants	Contaminant medium	Clay-biochar composite	Performance	Mechanism	References
Atenolol	Aqueous phase	KLN-pine chips	61–73% removal	Hydrophobic interaction and hydrogen bonding	Kim et al. [58]
Methylene blue	Aqueous phase	KLN, MMT-bagasse hickory	25.6–84.3% removal	Electrostatic interaction and ion exchange	Yao et al. [43]
Attrazene	Terrestrial	MMT-pig manure	114% sorption	Hydrophobic interaction, partitioning, and surface adsorption	Ren et al. [59]
Tetracycline	Aqueous phase	Red earth MMT-municipal solid waste	3.92–8.38 mg g^{-1} bio-sorption	Pore-filling, π–π interaction, ion exchange, and electrostatic interactions	Premarathna et al. [56]
Acetochlor	Aqueous phase	MMT-pine wood shaving	82.3–87.5% removal	Surface adsorption through π–π interaction	Li et al. [60]
Congo red	Aqueous phase	Bentonite-Kelp	24.2–33.3% removal	H-bonding, ion exchanges, and π–π interaction	Sewu et al. [61]
Sulfamethoxazole	Terrestrial	MMT-KLN-wheat straw	Sorption coefficient 6.12–7.18 L kg^{-1}	Partitioning and π–π EDA interaction	Zhao and Zhou [62]

(continued)

Table 2 (continued)

Contaminants	Contaminant medium	Clay-biochar composite	Performance	Mechanism	References
Norfloxacin	Aqueous phase	MMT-wheat straw	Adsorption 10.5–25.53 mg g^{-1}	Electrostatic interaction, H-bonding and pore-filling	Zhang et al. [29]
Indaziflam	Terrestrial	Natural soil-macadamia nut shell	Sorption coefficient 156–237 L kg^{-1}	Hydrophobic interactions	Trigo et al. [63]
17β-estradiol	Aqueous phase	MMT-cow manure wheat straw	Adsorption 41.02–62.89 mg g^{-1}	H-bonding	Tong et al. [64]

Table 3 Adsorptive capacity of clay-biochar composites for inorganic contaminants

Natural deposit	Biochar	Pretreatment condition	Environmental application	Enrichment mechanism	Performance	References
Attapulgite	Rice straw	Co-pyrolysis	Fixing As and Cd in sediments	Promote surface complexation	Adsorption of As and Cd by 82 and 48% from river sediments	Wang et al. [17]
MMT	Bark chip	Clay suspension and biochar	Restoration of Cu, Zn, and Pb contaminated soil	Promote cation exchange	Plummeting metal leaching by 100, 100, and 52% for Cu, Zn, and Pb	Arabyarmohammadi et al. [14]
MMT	Rice husk	Clay suspension and biochar	Immobilization of soil As	To provide silicon	73% removal of As from rice rhizosphere	Herath et al. [67]
MMT	Corn straw	Co-pyrolysis	Removal of Zn from aqueous phase	Cation exchange and surface complexation	Adsorption capacity 8.2 mg g^{-1}	Song et al. [68]
Struvite	Bamboo	Co-precipitation	To immobilize soil Cu	To provide PO_4^{3-} for Cu precipitation	47% removal of Cu	Li et al. [42]
Bentonite	Sweet sorghum bagasse	Co-pyrolysis	To remove Cr^{VI} and Zn^{II} from aqueous phase	Enhance surface adsorption	Adsorption capacity for Cr^{VI} and Zn^{II} 0.291–0.591 mg g^{-1}	Fosso-kankeu et al. [69]
MMT	Rice straw	Co-pyrolysis	To remove leached nitrate in water bodies	Electrostatic interaction, ion exchange, complexation, precipitation	Adsorption capacity for nitrate 5–9 mg g^{-1}	Viglašová et al. [66]

MMT = montmorillonite

Table 4 Application of biochar and composite biochar in mitigating gaseous emission in environment

Biochar type	Reduction in gaseous emission (%)				References
	CO_2	CH_4	N_2O	NH_3	
Wheat straw compost and bamboo wood biochar	5.5–72.6	12.5–72.9	19.0–77.4	12.4–81.6	Awasthi et al. [75]
Poultry waste and wheat straw	NA	20.5–61.5	19.2–48.1	4.7–15.1	Chen et al. [76]
Sawdust and pig manure	NA	15.5–26.1	9.2–24.8	NA	Chen et al. [15, 16]
Barley straw and poultry manure compost with hard wood and soft wood biochar composite	21.5–22.9	77.9–83.6	35.3–43.0	16.1–35.3	Chowdhury et al. [77]
Solid wet age waste and green waste compost with Holm oak biochar	52.9	95.1	NA	14.2	Vandecasteele et al. [78]
Sugarcane straw and poultry litter compost with poultry litter and green waste biochar composite	NA	77.8–83.3	54.9–60.2	68.2–74.9	Agyarko-Mintah et al. [79]
CO_2 sequestration (mmol g^{-1})					
CO_2 activated olive stones and almond shells biochar	CO_2 adsorption performance was better for biochar from olive stones at 25 °C (3 mmol g^{-1})				González et al. [80]
Hydrothermal carbonization of Jujun grass and Camellia japonica, and KOH/N_2 activation	CO_2 adsorption 3–21 mmol g^{-1}				Coromina et al. [81]

5 Future Research Challenges and Projections

This chapter provides evidence about production of biochar and clay-biochar composites and their soil application to improve soil physiochemical properties, soil productivity and overall soil health, to remove organic and inorganic pollutant toxicity and prominent impact of clay-biochar composites on easing climate change. Since many advantages of clay-biochar composites implication have been reported already, especially with remediation perspective, however, some limitations in implication still exist and research gaps need to be covered as well. In earlier studies, adsorption techniques were prominent practices focused to test clay-biochar composites efficiency in removing pollutants toxicity; however, some pilot-scale research work required to predict composite performance and maximum adsorption capacity in real environment. Additionally, several facts are needed to be further considered for clay-biochar industrial application and estimated cost should be considered as well, especially for contaminant remediation purpose. The production process of biochar and clay-biochar composites releases some airborne materials which should be considered as well. The complex process involved in manufacturing and modification of composites is costly and limited to its large scale application. More classified research is required for industrial and soil implication and composite stability after application and risk of secondary pollution should also be addressed as well.

Progressive efforts for developing efficient analytical techniques for accurate determination and reliable clay-biochar composites analyses should be focused. Additionally, feasible techniques should be employed for further modification to generate more efficient clay-biochar composite for remediation of broad range of contaminants. A comprehensive assessment must be done to for modification of single biochar with a number of clay minerals to observe broad picture and better insight to future application for multicomponent adsorption. In nutshell, such composite materials could provide excellent opportunity as future study and large scale environmental applications.

6 Conclusion

The production of clay-biochar composite reinforces each others performance as soil amendment and pollutants removal material as well as overcomes their limitation when applied individually. The resultant composite material showed significant impact in increasing surface functional groups, surface properties, overall porosity, and adsorptive characteristics. Green materials such as natural clay minerals as primary tamper agent on their combination with biochar (clay-biochar composite) prove useful in enhancing biochar performance at various angles such as improve soil quality and productivity, decrease pollutants mobility and plant availability, enhance soil moisture and water retention, limit greenhouse gases emission and their harmful effect and also revamp soil carbon sequestration. Undoubtedly, enhancing biochar performance by combination with natural clay minerals is a frontline in biochar study. Further advancement and expansion of scientific work in fabrication and suitable modification techniques and their enduring field application potentially anticipate a strategy headed for a viable forthcoming.

References

1. Rahman, M.M., Alam, K., Velayutham, E.: Is industrial pollution detrimental to public health? Evidence from the world's most industrialised countries. BMC Public Health **21**(1), 1–11 (2021)
2. Mojiri, A., Zhou, J.L., Robinson, B., Ohashi, A., Ozaki, N., Kindaichi, T., Farraji, H., Vakili, M.: Pesticides in aquatic environments and their removal by adsorption methods. Chemosphere **253** (2020)

3. Irshad, S., Liu, G., Yousaf, B., Ullah, H., Ali, M.U., Rinklebe, J.: Estimating the pollution characteristics and health risks of potentially toxic metal(loid)s in urbanindustrial soils in the Indus basin, Pakistan. Environ. Monit. Assess. **191** (2019)
4. Lwin, C.S., Seo, B.H., Kim, H.U., Owens, G., Kim, K.R.: Application of soil amendments to contaminated soils for heavy metal immobilization and improved soil quality—a critical review. Soil Sci. Plant Nutr. **64**(2), 156–167 (2018)
5. Srinivasan, R.: Advances in application of natural clay and its composites in removal of biological, organic, and inorganic contaminants from drinking water. Adv. Mater. Sci. Eng. (2011)
6. Thiebault, T.: Raw and modified clays and clay minerals for the removal of pharmaceutical products from aqueous solutions: state of the art and future perspectives. Crit. Rev. Environ. Sci. Technol. **50**, 1451–1514 (2020)
7. Khalfa, L., Sdiri, A., Bagane, M., Cervera, M.L.: A calcined clay fixed bed adsorption studies for the removal of heavy metals from aqueous solutions. J. Clean. Prod. **278**, 123935 (2021)
8. Liang, G., Wang, Z., Yang, X., Qin, T., Xie, X., Zhao, J., Li, S.: Efficient removal of oxytetracycline from aqueous solution using magnetic montmorillonite-BC composite prepared by one step pyrolysis. Sci. Total Environ. **695**, 133800 (2019). https://doi.org/10.1016/j.scitotenv.2019.133800
9. Lazaratou, C.V., Vayenas, D.V., Papoulis, D.: The role of clays, clay minerals and clay based materials for nitrate removal from water systems. Appl. Clay Sci. **185** (2020)
10. Wang, L., O'Connor, D., Rinklebe, J., Ok, Y.S., Tsang, D.C., Shen, Z., Hou, D.: Biochar aging: mechanisms, physicochemical changes, assessment, and implications for field applications. Environ. Sci. Technol. **54**(23), 14797–14814 (2020)
11. Krasucka, P., Pan, B., Sik Ok, Y., Mohan, D., Sarkar, B., Oleszczuk, P.: Engineered BC–a sustainable solution for the removal of antibiotics from water. Chem. Eng. J. **405**, 126926 (2021)
12. Kwiatkowski, M., Kalderis, D.: A complementary analysis of the porous structure of biochars obtained from biomass. Carbon Lett. **30**(3), 325–329 (2020)
13. Leng, L., Xiong, Q., Yang, L., Li, H., Zhou, Y., Zhang, W., Jiang, S., Li, H., Huang, H.: An overview on engineering the surface area and porosity of biochar. Sci. Total Environ. **763**, 144204 (2021)
14. Arabyarmohammadi, H., Darban, A.K., Abdollahy, M., Yong, R., Ayati, B., Zirakjou, A., van der Zee, S.E.: Utilization of a novel chitosan/clay/biochar nanobiocomposite for immobilization of heavy metals in acid soil environment. J. Polym. Environ. **26**(5), 2107–2119 (2018)
15. Chen, L., Chen, X.L., Zhou, C.H., Yang, H.M., Ji, S.F., Tong, D.S., Zhong, Z.K., Yu, W.H., Chu, M.Q.: Environmental-friendly montmorillonite-biochar composites: facile production and tunable adsorption-release of ammonium and phosphate. J. Clean. Prod. **156**, 648–659 (2017)
16. Chen, W., Liao, X., Wu, Y., Liang, J.B., Mi, J., Huang, J., Zhang, H., Wu, Y., Qiao, Z., Li, X., Wang, Y.: Effects of different types of biochar on methane and ammonia mitigation during layer manure composting. Waste Manag. **61**, 506–515 (2017)
17. Wang, X., Gu, Y., Tan, X., Liu, Y., Zhou, Y., Hu, X., Cai, X.X., Xu, W., Zhang, C., Liu, S.: Functionalized BC/clay composites for reducing the bioavailable fraction of arsenic and cadmium in river sediment. Environ. Toxicol. Chem. **38**, 2337–2347 (2019)
18. Hu, P., Zhang, Y., Liu, L., Wang, X., Luan, X., Ma, X., Chu, P.K., Zhou, J., Zhao, P.: Biochar/struvite composite as a novel potential material for slow release of N and P. Environ. Sci. Pollut. Res. **26**(17), 17152–17162 (2019)
19. Li, T., He, Y., Peng, X.: Efficient removal of tetrabromobisphenol A (TBBPA) using sewage sludge-derived BC: adsorptive effect and mechanism. Chemosphere **251** (2020)
20. Li, Y., Wang, X., Wang, Y., Wang, F., Xia, S., Zhao, J.: Struvite-supported biochar composite effectively lowers Cu bio-availability and the abundance of antibiotic-resistance genes in soil. Sci. Total Environ. **724**, 138294 (2020)
21. Mumme, J., Getz, J., Prasad, M., Lüder, U., Kern, J., Mašek, O., Buss, W.: Toxicity screening of biochar-mineral composites using germination tests. Chemosphere **207**, 91–100 (2018)

22. Hemingway, J.D., Rothman, D.H., Grant, K.E., Rosengard, S.Z., Eglinton, T.I., Derry, L.A., Galy, V.V.: Mineral protection regulates long-term global preservation of natural organic carbon. Nature **570**(7760), 228–231 (2019)
23. Mishra, G., Dash, B., Pandey, S.: Layered double hydroxides: a brief review from fundamentals to application as evolving biomaterials. Appl. Clay Sci. **153**, 172–186 (2018)
24. Yang, J.Q., Zhang, X., Bourg, I.C., Stone, H.A.: 4D imaging reveals mechanisms of clay-carbon protection and release. Nat. Commun. **12**, 622 (2021)
25. Aboudi Mana, S.C., Hanafiah, M.M., Chowdhury, A.J.K.: Environmental characteristics of clay and clay-based minerals. GeoloGy ecoloGy Landsc **1**(3), 155–161 (2017)
26. Awasthi, A., Jadhao, P., Kumari, K.: Clay nano-adsorbent: structures, applications and mechanism for water treatment. SN Appl. Sci. **1**(9), 1–21 (2019)
27. Shahadat, M., Isamil, S.: Regeneration performance of clay-based adsorbents for the removal of industrial dyes: a review. RSC Adv. **8**(43), 24571–24587 (2018)
28. Zhang, G., Lin, Y., Wang, M.: Remediation of copper polluted red soils with clay materials. J. Environ. Sci. **23**(3), 461–467 (2011)
29. Zhang, J., Lu, M., Wan, J., Sun, Y., Lan, H., Deng, X.: Effects of pH, dissolved humic acid and Cu^{2+} on the adsorption of norfloxacin on montmorillonite-BC composite derived from wheat straw. Biochem. Eng. J. **130**, 104–112 (2018)
30. Zotiadis, V., Argyraki, A.: Development of innovative environmental applications of attapulgite clay. Bull. Geol. Soc. Greece **47**(2), 992–1001 (2013)
31. Usman, A.R.A., Kuzyakov, Y., Stahr, K.: Effect of clay minerals on extractability of heavy metals and sewage sludge mineralization in soil. Chem. Ecol. **20**(2), 123–135 (2004)
32. Yi, X.U., Liang, X., Yingming, X.U., Xu, Q., Huang, Q., Lin, W., Yuebing, S.: Remediation of heavy metal-polluted agricultural soils using clay minerals: a review. Pedosphere **27**(2), 193–204 (2017)
33. Lehmann, J., Joseph, S. (eds.): Biochar for Environmental Management: Science, Technology and Implementation. Routledge (2015)
34. Sarmah, A.K., Srinivasan, P., Smernik, R.J., Manley-Harris, M., Antal, M.J., Downie, A., van Zwieten, L.: Retention capacity of biochar-amended New Zealand dairy farm soil for an estrogenic steroid hormone and its primary metabolite. Soil Res. **48**(7), 648–658 (2010)
35. Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S.: Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere **99**, 19–33 (2014)
36. Faiza, B., Gerhard, L.: Surface modification of clay minerals. Appl. Clay Sci. **19**(1), 3 (2001)
37. Kumari, N., Mohan, C.: Basics of clay minerals and their characteristic properties. Clay Clay Miner **24**, 1–29 (2021)
38. España, V.A.A., Sarkar, B., Biswas, B., Rusmin, R., Naidu, R.: Environmental applications of thermally modified and acid activated clay minerals: current status of the art. Environ. Technol. Innov. **13**, 383–397 (2019)
39. Toor, M., Jin, B.: Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing diazo dye. Chem. Eng. J. **187**, 79–88 (2012)
40. Vimonses, V., Lei, S., Jin, B., Chow, C.W., Saint, C.: Adsorption of congo red by three Australian kaolins. Appl. Clay Sci. **43**(3–4), 465–472 (2009)
41. Zhang, T., Wang, W., Zhao, Y., Bai, H., Wen, T., Kang, S., Song, G., Song, S., Komarneni, S.: Removal of heavy metals and dyes by clay-based adsorbents: From natural clays to 1D and 2D nano-composites. Chem. Eng. J. **420**, 127574 (2021)
42. Li, J., Wang, X., Zhao, G., Chen, C., Chai, Z., Alsaedi, A., Hayat, T., Wang, X.: Metal–organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions. Chem. Soc. Rev. **47**(7), 2322–2356 (2018)
43. Yao, Y., Gao, B., Fang, J., Zhang, M., Chen, H., Zhou, Y., Creamer, A.E., Sun, Y., Yang, L.: Characterization and environmental applications of clay-BC composites. Chem. Eng. J. **242**, 136–143 (2014)
44. Celis, R., Trigo, C., Facenda, G., Hermosín, M.D.C., Cornejo, J.: Selective modification of clay minerals for the adsorption of herbicides widely used in olive groves. J. Agric. Food Chem. **55**(16), 6650–6658 (2007)

45. Lehmann, J.: A handful of carbon. Nature **447**(7141), 143–144 (2007)
46. Gao, L., Goldfarb, J.L.: Characterization and adsorption applications of composite biochars of clay minerals and biomass. Environ. Sci. Pollut. Res. **28**(32), 44277–44287 (2021)
47. FAO: Status of the World's Soil Resources. FAO (2015)
48. Possinger, A.R., Zachman, M.J., Enders, A., Levin, B.D., Muller, D.A., Kourkoutis, L.F., Lehmann, J.: Organo–organic and organo–mineral interfaces in soil at the nanometer scale. Nat. Commun. **11**(1), 1–11 (2020)
49. Rafiq, M.K., Joseph, S.D., Li, F., Bai, Y., Shang, Z., Rawal, A., Hook, J.M., Munroe, P.R., Donne, S., Taherymoosavi, S., Mitchell, D.R.: Pyrolysis of attapulgite clay blended with yak dung enhances pasture growth and soil health: characterization and initial field trials. Sci. Total Environ. **607**, 184–194 (2017)
50. An, X., Wu, Z., Yu, J., Ge, L., Li, T., Liu, X., Yu, B.: High-efficiency reclaiming phosphate from an aqueous solution by bentonite modified biochars: a slow release fertilizer with a precise rate regulation. ACS Sustain. Chem. Eng. **8**(15), 6090–6099 (2020)
51. An, T., Cheng, H., Qin, Y., Su, W., Deng, H., Wu, J., Liu, Z., Guo, X.: The dual mechanisms of composite biochar and biofilm towards sustainable nutrient release control of phosphate fertilizer: effect on phosphorus utilization and crop growth. J. Clean. Prod. **311**, 127329 (2021)
52. An, X., Yu, J., Yu, J., Tahmasebi, A., Wu, Z., Liu, X., Yu, B.: Incorporation of biochar into semi-interpenetrating polymer networks through graft co-polymerization for the synthesis of new slow-release fertilizers. J. Clean. Prod. **272**, 122731 (2020)
53. Kárászová, M., Bourassi, M., Gaálová, J.: Membrane removal of emerging contaminants from water: which kind of membranes should we use? Membranes (Basel) **10**, 305 (2020)
54. Mian, M.M., Liu, G., Yousaf, B., Fu, B., Ullah, H., Ali, M.U., Abbas, Q., Mujtaba Munir, M.A., Ruijia, L.: Simultaneous functionalization and magnetization of BC via NH_3 ambiance pyrolysis for efficient removal of Cr (VI). Chemosphere **208**, 712–721 (2018)
55. Parlapiano, M., Akyol, Ç., Foglia, A., Pisani, M., Astolfi, P., Eusebi, A.L., Fatone, F.: Selective removal of contaminants of emerging concern (CECs) from urban water cycle via Molecularly Imprinted Polymers (MIPs): potential of upscaling and enabling reclaimed water reuse. J. Environ. Chem. Eng. **9**, 105051 (2021)
56. Premarathna, K.S.D., Rajapaksha, A.U., Adassoriya, N., Sarkar, B., Sirimuthu, N.M.S., Cooray, A., Ok, Y.S., Vithanage, M.: Clay-BC composites for sorptive removal of tetracycline antibiotic in aqueous media. J. Environ. Manag. **238**, 315–322 (2019)
57. Sizmur, T., Fresno, T., Akgül, G., Frost, H., Moreno-Jiménez, E.: Biochar modification to enhance sorption of inorganics from water. Biores. Technol. **246**, 34–47 (2017)
58. Kim, E., Jung, C., Han, J., Her, N., Min Park, C., Son, A., Yoon, Y.: Adsorption of selected micropollutants on powdered activated carbon and BC in the presence of kaolinite. Desalin. Water Treat. **57**, 27601–27613 (2016)
59. Ren, X., Wang, F., Zhang, P., Guo, J., Sun, H.: Aging effect of minerals on biochar properties and sorption capacities for atrazine and phenanthrene. Chemosphere **206**, 51–58 (2018)
60. Li, J., Li, S., Dong, H., Yang, S., Li, Y., Zhong, J.: Role of alumina and montmorillonite in changing the sorption of herbicides to BCs. J. Agric. Food Chem. **63**, 5740–5746 (2015)
61. Sewu, D.D., Lee, D.S., Tran, H.N., Woo, S.H.: Effect of bentonite-mineral co-pyrolysis with macroalgae on physicochemical property and dye uptake capacity of bentonite/biochar composite. J. Taiwan Inst. Chem. Eng. **104**, 106–113 (2019)
62. Zhao, Z., Zhou, W.: Insight into interaction between BC and soil minerals in changing BC properties and adsorption capacities for sulfamethoxazole. Environ. Pollut. **245**, 208–217 (2019)
63. Trigo, C., Spokas, K.A., Cox, L., Koskinen, W.C.: Influence of soil biochar aging on sorption of the herbicides MCPA, nicosulfuron, terbuthylazine, indaziflam, and fluoroethyldiaminotriazine. J. Agric. Food Chem. **62**(45), 10855–10860 (2014)
64. Tong, X., Jiang, L., Li, Y., Chen, X., Zhao, Y., Hu, B., Zhang, F.: Function of agricultural waste montmorillonite-BCs for sorptive removal of 17β-estradiol. Bioresour. Technol. **296**, 1–8 (2020)

65. Arif, M., Liu, G., Yousaf, B., Ahmed, R., Irshad, S., Ashraf, A., Zia-ur-Rehman, M., Rashid, M.S.: Synthesis, characteristics and mechanistic insight into the clays and clay minerals-biochar surface interactions for contaminants removal-a review. J. Clean. Prod. **310**, 127548 (2021)
66. Viglašová, E., Galamboš, M., Danková, Z., Krivosudský, L., Lengauer, C.L., Hood-Nowotny, R., Soja, G., Rompel, A., Matík, M., Briančin, J.: Production, characterization and adsorption studies of bamboo-based BC/montmorillonite composite for nitrate removal. Waste Manag. **79**, 385–394 (2018)
67. Herath, I., Zhao, F.J., Bundschuh, J., Wang, P., Wang, J., Ok, Y.S., Palansooriya, K.N., Vithanage, M.: Microbe mediated immobilization of arsenic in the rice rhizosphere after incorporation of silica impregnated biochar composites. J. Hazard. Mater. **398**, 123096 (2020)
68. Song, J., Zhang, S., Li, G., Du, Q., Yang, F.: Preparation of montmorillonite modified biochar with various temperatures and their mechanism for Zn ion removal. J. Hazard. Mater. **391**, 121692 (2020)
69. Fosso-kankeu, E., Waanders, F.B., Steyn, F.W.: The preparation and characterization of clay-BC composites for the removal of metal pollutants. In: 7th International Conference on Latest Trends in Engineering & Technology (ICLTET'2015) At Irene Pretoria South Africa, pp. 54–57 (2015). ISBN 978-9
70. Wang, L., Ok, Y.S., Tsang, D.C., Alessi, D.S., Rinklebe, J., Mašek, O., Bolan, N.S., Hou, D.: Biochar composites: emerging trends, field successes and sustainability implications. Soil Use Manag. **38**(1), 14–38 (2022)
71. Woolf, D., Amonette, J.E., Street-Perrott, F.A., Lehmann, J., Joseph, S.: Sustainable biochar to mitigate global climate change. Nat. Commun. **1**(1), 1–9 (2010)
72. Buss, W., Jansson, S., Wurzer, C., Mašek, O.: Synergies between BECCS and biochar—maximizing carbon sequestration potential by recycling wood ash. ACS Sustain. Chem. Eng. **7**(4), 4204–4209 (2019)
73. Rawal, A., Joseph, S.D., Hook, J.M., Chia, C.H., Munroe, P.R., Donne, S., Lin, Y., Phelan, D., Mitchell, D.R., Pace, B., Horvat, J.: Mineral–biochar composites: molecular structure and porosity. Environ. Sci. Technol. **50**(14), 7706–7714 (2016)
74. Ahmad, M., Ahmad, M., Usman, A.R., Al-Faraj, A.S., Abduljabbar, A., Ok, Y.S., Al-Wabel, M.I. Date palm waste-derived biochar composites with silica and zeolite: synthesis, characterization and implication for carbon stability and recalcitrant potential. Environ. Geochem. Health **41**(4), 1687–1704 (2019)
75. Awasthi, M.K., Duan, Y., Awasthi, S.K., Liu, T., Zhang, Z.: Influence of bamboo biochar on mitigating greenhouse gas emissions and nitrogen loss during poultry manure composting. Biores. Technol. **303**, 122952 (2020)
76. Chen, H., Awasthi, S.K., Liu, T., Duan, Y., Ren, X., Zhang, Z., Pandey, A., Awasthi, M.K.: Effects of microbial culture and chicken manure biochar on compost maturity and greenhouse gas emissions during chicken manure composting. J. Hazard. Mater. **389**, 121908 (2020)
77. Chowdhury, M.A., de Neergaard, A., Jensen, L.S.: Potential of aeration flow rate and biochar addition to reduce greenhouse gas and ammonia emissions during manure composting. Chemosphere **97**, 16–25 (2014)
78. Vandecasteele, B., Sinicco, T., D'Hose, T., Nest, T.V., Mondini, C.: Biochar amendment before or after composting affects compost quality and N losses, but not P plant uptake. J. Environ. Manag. **168**, 200–209 (2016)
79. Agyarko-Mintah, E., Cowie, A., Singh, B.P., Joseph, S., Van Zwieten, L., Cowie, A., Harden, S., Smillie, R.: Biochar increases nitrogen retention and lowers greenhouse gas emissions when added to composting poultry litter. Waste Manag. **61**, 138–149 (2017)
80. González, A.S., Plaza, M.G., Rubiera, F., Pevida, C.: Sustainable biomass-based carbon adsorbents for post-combustion CO_2 capture. Chem. Eng. J. **230**, 456–465 (2013)
81. Coromina, H.M., Walsh, D.A., Mokaya, R.: Biomass-derived activated carbon with simultaneously enhanced CO_2 uptake for both pre and post combustion capture applications. J. Mater. Chem. A **4**(1), 280–289 (2016)

Mitigation of Greenhouse Gas (GHG) Emissions Using Clay-Biochar Composites

Pelin Soyertaş Yapıcıoğlu and Mehmet İrfan Yeşilnacar

Abstract Biochar has attracted great attention recently due to its significant role in solving many environmental challenges. This chapter contains an overview of biochar derived clay composites applications for greenhouse gas (GHG) emissions. Biochar application is a potential method for reducing GHG emissions through carbon (C) sequestration and nitrous oxide (N_2O) mitigation. Especially, biochar application for the purposes of water and wastewater treatment could be regarded as a GHG mitigation technique in recent years. From this perspective, this chapter presented the GHG emission mitigation potential of clay-biochar composites. This study mainly concentrated on carbon dioxide (CO_2) and N_2O emissions reduction using this novel biochar type. This chapter mainly suggested on clay-biochar composites applications for GHG emissions reduction in water and wastewater. This study mainly concentrated on GHG emissions resulting from anaerobic wastewater treatment in this context, and this chapter contains the subtitles given below:

- GHG emissions mitigation using biochar
- GHG emissions reduction potential of clay-biochar composites
- GHG emission mitigation using clay-biochar composites in water and wastewater
- GHG emissions reduction potential of anaerobic wastewater treatment using clay-based biochar.

Keywords Clay-biochar · Greenhouse gas emissions · Reduction · Climate change · Water and wastewater treatment

---

P. Soyertaş Yapıcıoğlu · M. İ. Yeşilnacar (✉)
Engineering Faculty, Environmental Engineering Department, Harran University, Şanlıurfa, Turkey
e-mail: mirfan@harran.edu.tr

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_8

1 Introduction

Greenhouse gas emissions from water and wastewater treatment have been regarded as one of the main contributors to global warming [9, 21, 53, 55]. Majorly, carbon dioxide (CO_2) and nitrous oxide (N_2O) have been released from water and wastewater treatment processes [21]. Some technologies and reduction policies have been developed to mitigate GHG emissions from water and wastewater treatment [56]. GHG storage systems, carbon capture systems, designs and experiments based on biomimicry, using renewable energy sources, green bind applications, process modifications, innovative low-carbon water, and wastewater treatment processes (biochar applications, microalgal treatment, etc.), and optimization of operational conditions have been considered as the main GHG emissions mitigation techniques for water and wastewater treatment sector [53, 55]. Also, some new policies and strategies have been declared for the reduction of GHG emissions [21]. European Union (EU) Green Deal is the new growth strategy of the European Union (EU) that includes the main aims of zeroing net greenhouse gas emissions by 2050 and ending the dependence of economic growth on resource use [11]. With the EU Green Deal, a strategy has been proposed that envisages zeroing the greenhouse gas (GHG) emissions of the EU industry by 2050. Among the research topics within the framework of adaptation to the Green Deal, the major topic has been considered as "Climate Change, Environment and Biodiversity: Studies to Contribute to the Aim of Regulation of Climate Change, Carbon Emissions and Greenhouse Gas Emissions". According to the statement, GHG emissions should be mitigated in considerable quantities, and this mitigation of GHG emissions could lead to economic wealth all over the world [11]. According to the EU Green Deal fit for 55 packages [10], approximately 40% of mitigation should be ensured for the water and waste sector by 2030 [56]. Water and wastewater collection and treatment sector has been regarded as one of the main GHG emissions resources [20, 54]. In this context, some regulations and technical control strategies should be enhanced and declared to reduce GHG emissions from water and wastewater treatment sector.

There are several GHG mitigation methods such as modification of process configurations and conditions, microalgal treatment methods, usage of renewable energy resources for water and wastewater systems. Amon them, renewable energy applications have been preferred commonly by water sector authorities [57, 61]. Furthermore, biomass energy could be an efficient mitigation way due to many advantages. These advantages could be considered that biomass energy is cheaper and feasible for application in the water and wastewater treatment plants [12, 25]. Among types of biomass energy, biochar application is commonly used for greenhouse gas emission mitigation at water and wastewater treatment plants [5, 27, 65]. It is generally applied since biochar application is known also a water and wastewater treatment technique [18, 45, 46].

Biochar is a carbon-rich substance which could be derived from various organic and inorganic waste feedstocks. Biochar has gained raising significance because of its unique natural stable structure such as high carbon content and ion exchange capacity and large surface area [33, 47]. Biochar has attracted great attention in recent years due to its important role in solving many environmental problems and challenges [33]. It is less expensive than other treatment methods and can immediately adsorb greenhouse gas emissions from water and wastewater [34, 36, 57]. Biochar, a carbon-rich substance generated from the pyrolysis or carbonization of biomass wastes, is a crucial substance of interest as it could remove pollutants and applied as a negative carbon emission technology [24, 33, 57, 59]. Many research have confirmed that the addition of clay during the pyrolysis of biomass is beneficial for the generation of biochar with a high stability [15, 58]. Carbon dioxide (CO_2) and nitrous oxide (N_2O) are the main greenhouse gases from water and wastewater treatment which could be adsorbed by clay-based biochar [44]. It is known that the stability of biochar is a significant parameter to measure the capacity of biochar for carbon sequestration [58].

From this point of view, this chapter aimed that CO_2 and N_2O emissions reduction using this novel biochar type (clay-based biochar). Also, this chapter mainly recommended on clay-biochar composites applications for GHG emissions reduction in water and wastewater.

2 GHG Emissions Mitigation Using Biochar

Biochar is a porous carbonaceous substance with large specific surface area, and it is generated with the help pyrolysis of biomass in sealed containers, under limited oxygen environment [32]. Biochar is generated by pyrolysis of biomass such as agricultural crops, fertilizers, and solid wastes [36, 57, 59]. Traditionally biochar is applied for carbon sequestration due to its adsorption capacity in water and wastewaters so it could be a greenhouse gas mitigation technique [33, 53].

Biochar resolves unstable organic carbon in biomass into inorganic carbon, while ensuring long-term carbon sequestration and mitigating the net GHG emissions [41]. The modification of biochar with clay minerals could enhance the pyrolysis process of biomass, raise the stage of aromatic condensation, and also mitigate the oxidation of biochar, so the stability of biochar has been enhanced [58]. Clay minerals play role as a natural scavenger of contaminants in water and wastewater, through the uptake of cations and anions either through ion exchange or adsorption [2]. It could be considered that addition of clay into biochar could increase the adsorption capacity of pollutants and greenhouse gases. N_2O and CO_2 are regarded as the main greenhouse gases from water and wastewater treatment processes [54].

The mechanism of biochar to remove nitrous oxide is as follows: Denitrification is an important mechanism to reduce nitrate (NO_3) in water and wastewater. The biochar is thought to act as an electron shuttle to reduce N_2O. Biochar is a persistent compound that could remain in water for many years. N_2O is produced by microorganisms through nitrification and denitrification. Biochar quickly adsorbs ammonia from the soil and acts as a buffer, thus indirectly reducing ammonia evaporation [33]. This may also carry out to the aquatic environment. In addition, the biochar is an effective adsorber of dissolved ammonium and nitrate, which causes nitrous oxide emissions to the atmosphere [3]. Therefore, biochar application might be a possible method for N_2O reduction in water. Water and wastewater treatment plants have been regarded as one of the most significant sources of indirect greenhouse gas emissions [21]. Methodologies on this subject are inadequate and open to development.

Water supplies may contain CO_2 due to its geogenic structure and water-rock interactions. Carbonic acid is formed due to the dissolution of CO_2 in water, which turns into bicarbonate (HCO_3^-) and this is a two-way reaction. When water is exposed to the atmosphere, CO_2 is released into the atmosphere and calcite ($CaCO_3$) precipitates. For this reason, it is predicted that CO_2 emissions may occur due to the treatment of groundwater. Due to the carbon sequestration capacity of the biochar, it can adsorb CO_2 emissions [33]. Studies are generally aimed at the removal of CO_2 emissions originating from the soil with biochar. It is foreseen in this direction that the CO_2 emission arising from the treatment of water will be captured by the biochar. It is known that biochar will greatly affect the carbon dynamics in groundwater and store carbon in its body. CO_2 emissions also could be considered to be originated by respiration of aerobic biomass and living organisms in wastewater [53]. CO_2 emission in wastewater could be released that the materials which cannot settle with the help of flocculation process [53].

From this perspective, clay-based biochar could adsorb N_2O and CO_2 immediately from water and wastewater. This chapter contains an overview of biochar derived clay composites applications for GHG emissions from water and wastewater.

3 GHG Emissions Reduction Potential of Clay-Biochar Composites in Water and Wastewater

In the literature, there are studies on reducing N_2O emission from the soil with the addition of biochar [33]. In terms of water and wastewater treatment, there are only a limited number of studies on the minimization of N_2O from water and wastewater using biochar derived biomass. Table 1 shows the studies on N_2O emissions reduction potential of clay-biochar composites in water and wastewater. There are limited studies in the literature related to CO_2 mitigation using biochar. Biochar application is a novel and recent treatment technique for water and wastewater [57]. The possible schematic theme of this chapter for CO_2 and N_2O uptake of clay-biochar composites is given in Fig. 1.

Biochar is a porous carbonaceous substance with a large specific surface area generated by the pyrolysis which comprises of carbon and mineral fractions. It is known that generating biochar-based composites enables to combine the advantages of biochar with additive minerals, which the resulting composites usually raises the removal efficiency in functional groups, pore properties, surface area, and catalytic degradation ability [60]. Adsorption is the major mechanism for biochar to remove

Table 1 N_2O emissions reduction potential of biochar composites in water and wastewater

Reference	Type of biochar	Case study
Sun et al. [44]	Sewage sludge	At wastewater filtration, it has been determined that lower N_2O emission is released with the application of biochar
Zhou et al. [65]	Bamboo	It has been determined that lower N_2O emissions occur with the application of biochar in the constructed wetland
Bock et al. [4]	Wood chips	It was determined that the N_2O emission decreased with the addition of biochar in the wastewater bioreactor
Guo et al. [18]	Cattail	It has been confirmed that N_2O emission could be reduced with increasing biochar dose in constructed wetland
Liang et al. [25]	Bamboo	It has been reported that the N_2O emission decreased by 56.0–67.5% with the addition of biochar in a constructed wetland where wastewater is treated
Zhou et al. [66]	Bamboo	It has been determined that the N_2O emission is reduced by 20% with the addition of biochar in the constructed wetland where domestic wastewater is treated
Zheng et al. [64]	Corn stalk	It has been determined that the N_2O emission resulting from the treatment of synthetic wastewater is reduced by biochar
Ji et al. [22]	Tree branch	It has been proven that N_2O emission can be reduced by increasing biochar application in constructed wetland
Feng et al. [12]	Bamboo	It has been proven that N_2O emission can be reduced with increasing biochar dose in constructed wetland

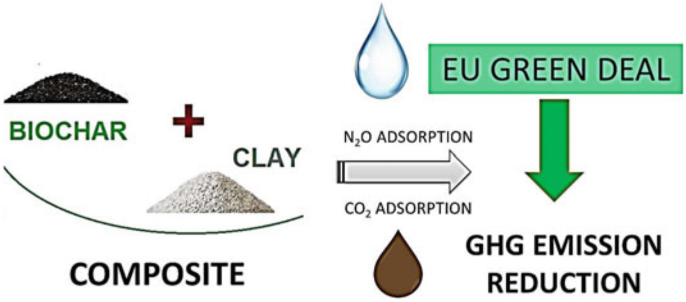


Fig. 1 Schematic summary of the study

contaminants and GHG emissions. The adsorption capacity of biochar has corresponded to its surface area, pore size, functional groups, and ion exchange capacity [47]. Biochar has been modified with acids, metal ions, and alkali and oxidizing substances to amend the physicochemical properties [1]. Clay addition to biochar has increased the pore size, and it leads to higher adsorption capacity. Clay-biochar composite is generated while mixing the raw biomass before pyrolysis or the mixing of produced biochar with clay minerals [6]. This composite has been defined by high porosity and a considerable compatibility with water pollutants [14]. From this point of view, clay addition to biochar could be a good alternative for reducing GHG emissions from water and wastewater. [62] reported that clay-mineral modification enhanced that organomineral layer of clay raises the biochar stability when biochar is applied to soil [62]. Yao et al. [52] revealed that clay particles increase the adsorption capacity of biochar. This novel biochar type could be similarly used for N_2O and CO_2 adsorption from water and wastewater.

Surface modification has been used to generate biochar-based materials, particularly biochar-based composites with improved functions for many purposes [52]. In clay-based composites, the biochar is the porous structure to serve the distribution of the nanoparticles. This specification could be considered for the generation of a novel kind of engineered biochar with clay particles has high sorption ability [52]. These composites have unique characteristics and functions inherited from both clay and biochar which could be carried out since the feedstock materials are effective and cheaper.

These clay-biochar composites have higher potential to be used as a novel and low-cost adsorbent for water and wastewater treatment, especially for the removal of pollutants. Furthermore, due to the synthesis and low-cost, clay-biochar composites could also be used in to improve water quality and carbon sequestration. The stability of biochar is an important indicator in determining the potential of biochar for carbon sequestration. It is known that addition of clay to biochar will increase the stability of the biochar. From this point of view, CO_2 adsorption using clay-based biochar would be more effective than using raw biochar. Due to nitrate removal by this novel biochar, also N_2O emissions reduction has been indirectly achieved. The adsorbent specifications of clays could be enhanced by different amendments, and higher contaminant adsorption is determined in modified clays than that in natural clays. Premarathna et al. [32] investigated antibiotics removal from water using clay-based biochar. They reported that higher adsorption efficiency while using clay-biochar composites. The restricted studies on this topic have confirmed that clay-biochar composites have better performance than raw biochar for water and wastewater treatment due to their stability and adsorption capacity. Indirectly, this specific qualification might accelerate the GHG adsorption capacity from water and wastewater. N_2O and CO_2 would uptake in larger amounts from water and wastewater when clay-biochar composites are applied.

The amount of GHG emissions has varied according to applied water and wastewater treatment process. In this context, direct GHG emissions have been resulted due to the treatment process [31]. Among them, anaerobic treatment is widely used technique for wastewater treatment. In the end of this process, biogas is a mixture of the important greenhouse gases which are CO_2 and methane (CH_4) is released to the atmosphere [16, 17, 29]. The addition of clay-based biochar to this process could decrease the GHG emissions from anaerobic wastewater configurations. Also, biogas treatment is very important topic to deal with the disadvantages of anaerobic wastewater treatment. Especially, clay-based biochar could be applied for desulphurization process of biogas.

4 GHG Emissions Reduction Potential of Anaerobic Wastewater Treatment Using Clay-Based Biochar

Anaerobic treatment is the conversion of microorganisms into other products and by-products in the absence of oxygen and in the presence of anaerobic microorganisms [13, 29]. Biogas management is an environmental and economic challenge resulted from anaerobic treatment [29]. From this point of view, biochar application which is cheaper and innovative method could be an alternative technique for biogas desulphurization (H_2S removal) and GHG emissions mitigation. It contains mainly CO_2, $CH_{4,}$ and hydrogen sulfide (H_2S). This chapter recommended on clay-based biochar application for the reduction of GHG emissions and biochar desulphurization process. Biochar adsorption process has carried out for the H_2S removal from biogas in recent years [7, 30, 38, 43, 67].

H_2S is often associated with the smell of rotten eggs which is a colorless, heavier than air, poisonous, and corrosive gas [13, 29, 49]. When released into the environment, hydrogen sulfide disperses into the air and forms sulfur dioxide (SO_2) and sulfuric acid. It is estimated that H2S remains in the atmosphere for about 18 h. SO_2 is regarded as an indirect greenhouse gas as it forms aerosols when combined with elemental carbon. Surprisingly, aerosols contribute to both cooling and warming of the earth. Although H_2S is not a direct greenhouse gas, it is considered an indirect greenhouse gas since it is the source of SO_2 in the atmosphere [21]. Also, H_2S has the significant poison effect to fauna and flora and human health [63]. SO_2 is formed by the oxidation of H_2S, and it is an indirect greenhouse gas with the limit concentration of 150 μgm^{-3} 24^{-h} [49]. H_2S comprises 0–3% of biogas which is the undesirable component of biogas [29]. H_2S leads to a significant maintenance requirement at anaerobic wastewater configurations [13]. In this case, H_2S should be removed from biogas using effective treatment methods. Adsorption and absorption have been applied for H_2S removal [13]. Adsorption is regarded as the best technique for H_2S removal due to its main operation, minimum operational cost, and higher removal efficiency [28]. The main adsorbent is activated carbon generated from petroleum which is non-renewable. In last decades, biochar derived from waste biomass materials which are renewable, less expensive, and sustainability has been applied for this purpose [28]. So, biochar could be an innovative and alternative technique for biogas treatment in terms of H_2S removal. Cost-effective H_2S removal agents derived from many feedstocks could be supported by clay which is the name under the clay-based biochar.

In this context, biochar adsorption process, which is a cheap and innovative method, can be a unique method and solution for H_2S removal from anaerobic wastewater treatment due to its many advantages. Clay addition could improve the H_2S adsorption capacity of the biochar. In the literature, related studies were investigated using Web of Science (WOS) data base. Table 2. shows the details about H_2S removal from biogas using various biochar feedstocks.

Table 2 H_2S removal using biochar

Reference	Type of biochar	Biochar production technique	Case study/removal efficiency
Choudhury and Lansing [7]	Corncob and maple (Fe catalyzed)	Pyrolysis	H_2S removal from biogas resulting from anaerobic decomposition (90.5% of H_2S removal)
Scheufele et al. [40]	Babassu	Pyrolysis, fixed bed column	A new mathematical model was developed to remove H_2S using a new type of biochar
Sahota et al. [37]	Leaf	Carbonization (200, 300, and 400 °C)	H_2S removal from biogas, (84.2% of H_2S removal at 400 °C)
Kanjanarong et al. [23]	Wood sawdust and anaerobic sludge	Continuous fluid pyrolytic reactor, Continuous stirred-tank reactor (CSTR), 600 °C	H_2S removal resulting from anaerobic wastewater treatment (98% of H_2S removal efficiency)
Oliveira et al. [30]	Soft and hard tree	Pyrolysis, CSTR (in the range of 550 and 800 °C)	H_2S removal resulting from anaerobic wastewater treatment (>98% removal efficiency)
Das et al. [8]	Compost and spruce	Pyrolysis, 650 °C	H_2S removal from anaerobic filter (70% of H_2S removal)
Xu et al. [50]	Pig manure and sludge	Slow pyrolysis	Pig manure adsorbs H_2S more effectively than treatment sludge-based biochar
Han et al. [19]	Macroalgae	Pyrolysis	H_2S removal from biogas (40–60% of H_2S removal efficiency)
Li et al. [26]	Sewage sludge	Microwave supported pyrolysis, 650 °C	78.4% of H_2S removal efficiency
Yang et al. [51]	Reed black liquor	Fast pyrolysis, 500 °C	60 mg/gH_2S of removal capacity
Ma et al. [28]	Nitrogen-based plant (sawdust)	Co-pyrolysis (in the range of 600–900 °C)	54.8 mg/gH_2S of removal capacity
Su et al. [42]	Coconut shell and various animal manures	Pyrolysis, 750 °C	38.73 mgH_2S/g biochar of removal efficiency
Ro et al. [35]	Pine tree	Pyrolysis, 500–600 °C	2.51 mg/g H_2S of removal efficiency
Zhu et al. [67]	Wood, sewage sludge, activated ash	Pyrolysis, 450–700 °C	H_2S removal from biogas (2.2–3.22 mg/g H_2S of removal efficiency)

(continued)

Table 2 (continued)

Reference	Type of biochar	Biochar production technique	Case study/removal efficiency
Wang et al. [48]	Poplar sawdust	Pyrolysis	H_2S removal from biogas (%78 of H_2S removal)
Seo et al. [39]	Rice shell	Pyrolysis, 400–500 °C	24.41 mg/g H_2S of removal efficiency
Sawalha et al. [38]	Almond shells, eucalyptus and coffee granules	Pyrolysis, 500 °C	H_2S removal from biogas, almond shell (690 mg H_2S/g adsorbent), eucalyptus (230 mg H_2S/g adsorbent), and coffee granules (22 mg H_2S/g adsorbent)

As seen from Table 2, H_2S removal with biochar is generally applied for the purpose of removing H_2S from biogas (desulphurization). Pyrolysis is the frequently applied production technique. From this perspective, clay-based biochar could be an effective material for H_2S removal from biogas.

5 Conclusions

This chapter recommended that biochar derived clay composites applications for greenhouse gas emissions. Furthermore, biochar application for the purposes of water and wastewater treatment could be considered as a greenhouse gas emission mitigation technique, recently. Also, this chapter mainly focused on clay-biochar composites applications for GHG emissions reduction in water and wastewater. It might be possible to reduce N_2O and CO_2 emissions in water and wastewater using clay-biochar composites. The limited numbers of studies on this topic have confirmed that clay-biochar composites have better performance than raw biochar for water and wastewater treatment due to their stability and adsorption capacity. The stability of biochar is a significant parameter in defining the potential of biochar for carbon sequestration and greenhouse gas emission uptake. It is confirmed in many studies that addition of clay to biochar will increase the stability of the biochar.

Also, H_2S removal from biogas which is the end-product of anaerobic wastewater treatment is possible using various types of biochar in the literature. H_2S is regarded as also an indirect greenhouse gas recently. Clay addition could improve the adsorption capacity and stability of biochar for more effective H_2S removal from biogas. This chapter also recommended that the application of clay-based biochar for desulphurization.

In our future work, the feasibility of this strategy for improving the stability of biochar with clay addition for CO_2 and N_2O emissions from water and wastewater will be investigated. This application is a novel research topic for GHG emissions reduction, so the studies in this topic will be increased in near future. Also, H_2S removal of biogas using clay-based biochar would be experienced in the near future. This review chapter could be a guide for the new research about this topic.

References

1. Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., Chen, M.: Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. Biores. Technol. **214**, 836–851 (2016)
2. Atasoy, A.D., Bilgic, B.: Adsorption of copper and zinc ions from aqueous solutions using montmorillonite and bauxite as low-cost adsorbents. Mine Water Environ. **37**, 205–210 (2018)
3. Awasthi, M.K., Wang, Q., Huang, H., Ren, X., Lahori, A.H., Mahar, A., Zhang, Z.: Influence of zeolite and lime as additives on greenhouse gas emissions and maturity evolution during sewage sludge composting. Biores. Technol. **216**, 172–181 (2016)
4. Bock, E.M., Coleman, B.S., Easton, Z.M.: Effect of biochar, hydraulic residence time, and nutrient loading on greenhouse gas emission in laboratory-scale denitrifying bioreactors. Ecol. Eng. **120**, 375–383 (2018)
5. Capodici, M., Avona, A., Laudicina, V.A., Viviani, G.: Biological groundwater denitrification systems: lab-scale trials aimed at nitrous oxide production and emission assessment. Sci. Total Environ. **630**, 462–468 (2018)
6. Cheng, N., Wang, B., Wu, P., Lee, X., Xing, Y., Chen, M., Gao, B.: Adsorption of emerging contaminants from water and wastewater by modified biochar: a review. Environ. Pollut. **273**, 116448 (2021)
7. Choudhury, A., Lansing, S.: Biochar addition with Fe impregnation to reduce H_2S production from anaerobic digestion. Biores. Technol. **306**, 123121 (2020)
8. Das, J., Rene, E.R., Dupont, C., Dufourny, A., Blin, J., van Hullebusch, E.D.: Performance of a compost and biochar packed biofilter for gas-phase hydrogen sulfide removal. Biores. Technol. **273**, 581–591 (2019)
9. Demir, Ö., Yapıcıoğlu, P.: Investigation of GHG emission sources and reducing GHG emissions in a municipal wastewater treatment plant. Greenh. Gases: Sci. Technol. **9**(5), 948–964 (2019)
10. European (EU) Commission, European Green Deal 2021 Fit for 55 Package: The EU's Fit for 55 Package—Key Takeaways From Bernstein Renewables, Chemical, Airlines & Energy Teams (2021)
11. European (EU) Commission, Communication from the Commission to the European Parliament, the 533 European Council, the Council, the European Economic and Social Committee and the 534 Committee of the Regions–The European Green Deal (2019)
12. Feng, Y., Li, D., Sun, H., Xue, L., Zhou, B., Yang, L., Xing, B.: Wood vinegar and biochar co-application mitigates nitrous oxide and methane emissions from rice paddy soil: a two-year experiment. Environ. Pollut. **267**, 115403 (2020)
13. Filibeli, A., Büyükkamacı, N., Ayol, A.: Anaerobic Treatment, 2nd edn. Dokuz Eylül Engineering Faculty Publication, İzmir (2009)
14. Fu, C., Zhang, H., Xia, M., Lei, W., Wang, F.: The single/co-adsorption characteristics and microscopic adsorption mechanism of biochar-montmorillonite composite adsorbent for pharmaceutical emerging organic contaminant atenolol and lead ions. Ecotoxicol. Environ. Saf. **187**, 109763 (2020)
15. Grutzmacher, P., Puga, A.P., Bibar, M.P.S., Coscione, A.R., Packer, A.P., de Andrade, C.A.: Carbon stability and mitigation of fertilizer induced N_2O emissions in soil amended with biochar. Sci. Total Environ. **625**, 1459–1466 (2018)
16. Gülşen, H., Yapıcıoğlu, P.: Minimizing greenhouse gas emissions from leachate treatment by using zeolite column. Carbon Manag. **12**(1), 51–68 (2021)

17. Gülşen, H., Yapıcıoğlu, P.: Greenhouse gas emission estimation for a UASB reactor in a dairy wastewater treatment plant. Int. J. Glob. Warm. **17**(4), 373–388 (2019)
18. Guo, F., Zhang, J., Yang, X., He, Q., Ao, L., Chen, Y.: Impact of biochar on greenhouse gas emissions from constructed wetlands under various influent chemical oxygen demand to nitrogen ratios. Biores. Technol. **303**, 122908 (2020)
19. Han, X., Chen, H., Liu, Y., Pan, J.: Study on removal of gaseous hydrogen sulfide based on macroalgae biochars. J. Nat. Gas Sci. Eng. **73**, 103068 (2020)
20. IPCC Fifth Assessment Report: Climate Change 2014: Mitigation of Climate Change. Cambridge University Press, Cambridge, England (2014)
21. IPCC Sixth Assessment Report, Climate Change 2022: impacts, Adaptation and Vulnerability, Cambridge, England (2022)
22. Ji, B., Chen, J., Li, W., Mei, J., Yang, Y., Chang, J.: Greenhouse gas emissions from constructed wetlands are mitigated by biochar substrates and distinctly affected by tidal flow and intermittent aeration modes. Environ. Pollut. **271**, 116328 (2021)
23. Kanjanarong, J., Giri, B.S., Jaisi, D.P., Oliveira, F.R., Boonsawang, P., Chaiprapat, S., Khanal, S.K.: Removal of hydrogen sulfide generated during anaerobic treatment of sulfate-laden wastewater using biochar: evaluation of efficiency and mechanisms. Biores. Technol. **234**, 115–121 (2017)
24. Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Hockaday, W.C., Crowley, D.: Biochar effects on soil biota—A review. Soil Biol. Biochem. **43**(9), 1812–1836 (2011)
25. Liang, Y., Wang, Q., Huang, L., Liu, M., Wang, N., Chen, Y.: Insight into the mechanisms of biochar addition on pollutant removal enhancement and nitrous oxide emission reduction in subsurface flow constructed wetlands: microbial community structure, functional genes and enzyme activity. Biores. Technol. **307**, 123249 (2020)
26. Lin, Q., Zhang, J., Yin, L., Liu, H., Zuo, W., Tian, Y.: Relationship between heavy metal consolidation and H2S removal by biochar from microwave pyrolysis of municipal sludge: effect and mechanism. Environ. Sci. Pollut. Res. **28**(22), 27694–27702 (2021)
27. Liu, Y., Ngo, H.H., Guo, W., Zhou, J., Peng, L., Wang, D., Ni, B.J.: Optimizing sulfur-driven mixotrophic denitrification process: system performance and nitrous oxide emission. Chem. Eng. Sci. **172**, 414–422 (2017)
28. Ma, Q., Chen, W., Jin, Z., Chen, L., Zhou, Q., Jiang, X.: One-step synthesis of microporous nitrogen-doped biochar for efficient removal of CO_2 and H_2S. Fuel **289**, 119932 (2021)
29. Metcalf and Eddy.: Wastewater Engineering: treatment and Resource Recovery, 5th ed., McGraw-Hill International Editions (2014)
30. Oliveira, F.R., Surendra, K.C., Jaisi, D.P., Lu, H., Unal-Tosun, G., Sung, S., Khanal, S.K.: Alleviating sulfide toxicity using biochar during anaerobic treatment of sulfate-laden wastewater. Biores. Technol. **301**, 122711 (2020)
31. Parravicini, V., Svardal, K., Krampe, J.: Greenhouse gas emissions from wastewater treatment plants. Energy Procedia **97**, 246–253 (2016)
32. Premarathna, K.S.D., Rajapaksha, A.U., Adassoriya, N., Sarkar, B., Sirimuthu, N.M., Cooray, A., Vithanage, M.: Clay-biochar composites for sorptive removal of tetracycline antibiotic in aqueous media. J. Environ. Manag. **238**, 315–322 (2019)
33. Qambrani, N.A., Rahman, M.M., Won, S.: Biochar properties and eco-friendly applications for climate change mitigation, waste management, and wastewater treatment: a review. Renew. Sustain. Energy Rev. **79**, 255–273 (2017)
34. Rajapaksha, A.U., Chen, S.S., Tsang, D.C., Zhang, M., Vithanage, M., Mandal, S., Ok, Y.S.: Engineered/designer biochar for contaminant removal/immobilization from soil and water: potential and implication of biochar modification. Chemosphere **148**, 276–291 (2016)
35. Ro, K.S., Woodbury, B., Spiehs, M., Szogi, A.A., Silva, P.J., Hwang, O., Cho, S.: Pilot-scale H2S and swine odor removal system using commercially available biochar. Agronomy **11**(8), 1611 (2021)
36. Sadhu, M., Bhattacharya, P., Vithanage, M., Sudhakar, P.P.: Adsorptive removal of fluoride using biochar—A potential application in drinking water treatment. Sep. Purif. Technol. 119106 (2021)

37. Sahota, S., Vijay, V.K., Subbarao, P.M.V., Chandra, R., Ghosh, P., Shah, G., Thakur, I.S.: Characterization of leaf waste based biochar for cost effective hydrogen sulphide removal from biogas. Biores. Technol. **250**, 635–641 (2018)
38. Sawalha, H., Maghalseh, M., Qutaina, J., Junaidi, K., Rene, E.R.: Removal of hydrogen sulfide from biogas using activated carbon synthesized from different locally available biomass wastes-a case study from Palestine. Bioengineered **11**(1), 607–618 (2020)
39. Seo, D.C., Guo, R., Lee, D.H.: Performance of alkaline impregnated biochar derived from rice hull for hydrogen sulfide removal from gas. Environ. Eng. Res. **26**(6) (2021)
40. Scheufele, F.B., da Silva, E.S., Cazula, B.B., Marins, D.S., Sequinel, R., Borba, C.E., Alves, H.J.: Mathematical modeling of low-pressure H2S adsorption by babassu biochar in fixed bed column. J. Environ. Chem. Eng. **9**(1), 105042 (2021)
41. Sewu, D.D., Lee, D.S., Tran, H.N., Woo, S.H.: Effect of bentonite-mineral co-pyrolysis with macroalgae on physicochemical property and dye uptake capacity of bentonite/biochar composite. J. Taiwan Inst. Chem. E **104**, 106–113 (2019)
42. Su, L., Chen, M., Zhuo, G., Ji, R., Wang, S., Zhang, L., Li, H.: Comparison of biochar materials derived from coconut husks and various types of livestock manure, and their potential for use in removal of H2S from biogas. Sustainability **13**(11), 6262 (2021)
43. Sun, Y., Yang, G., Zhang, L., Sun, Z.: Preparation of high performance H_2S removal biochar by direct fluidized bed carbonization using potato peel waste. Process Saf. Environ. Prot. **107**, 281–288 (2017)
44. Sun, Y., Qi, S., Zheng, F., Huang, L., Pan, J., Jiang, Y., Xiao, L.: Organics removal, nitrogen removal and N2O emission in subsurface wastewater infiltration systems amended with/without biochar and sludge. Biores. Technol. **249**, 57–61 (2018)
45. Vithanage, M., Herath, I., Joseph, S., Bundschuh, J., Bolan, N., Ok, Y.S., Rinklebe, J.: Interaction of arsenic with biochar in soil and water: a critical review. Carbon **113**, 219–230 (2017)
46. Vithanage, M., Rajapaksha, A.U., Tang, X., Thiele-Bruhn, S., Kim, K.H., Lee, S.E., Ok, Y.S.: Sorption and transport of sulfamethazine in agricultural soils amended with invasive-plant-derived biochar. J. Environ. Manag. **141**, 95–103 (2014)
47. Wang, J., Wang, S.: Preparation, modification and environmental application of biochar: a review. J. Clean. Prod. **227**, 1002–1022 (2019)
48. Wang, H., Larson, R.A., Runge, T.: Impacts to hydrogen sulfide concentrations in biogas when poplar wood chips, steam treated wood chips, and biochar are added to manure-based anaerobic digestion systems. Bioresour. Technol. Report. **7**, 100232 (2019)
49. World Health Organization (WHO).: Air Quality Guidelines, Second Edition, Chapter 6.6 (2000)
50. Xu, X., Cao, X., Zhao, L., Sun, T.: Comparison of sewage sludge-and pig manure-derived biochars for hydrogen sulfide removal. Chemosphere **111**, 296–303 (2014)
51. Yang, G., Sun, Y., Zhang, J.P., Wen, C.: Fast carbonization using fluidized bed for biochar production from reed black liquor: optimization for H_2S removal. Environ. Technol. **37**(19), 2447–2456 (2016)
52. Yao, Y., Gao, B., Fang, J., Zhang, M., Chen, H., et al.: Characterization and environmental applications of clay-biochar composites. Chem. Eng. J. **242**, 136–143 (2014)
53. Yapıcıoğlu, P.: Greenhouse gases emissions minimization of wastewater treatment plants. M.Sc. thesis. Harran University Graduate School of Natural and Applied Science, Şanlıurfa, Türkiye (2018)
54. Yapıcıoğlu, P.: Minimization of greenhouse gas emissions from extended aeration activated sludge process. Water Pract. Technol. **16**(1), 96–107 (2021)
55. Yapıcıoğlu, P., Demir, Ö.: Minimizing greenhouse gas emissions of an industrial wastewater treatment plant in terms of water—Energy nexus. Appl. Water Sci. **11**(12), 1–14 (2021)
56. Yapıcıoğlu, P., Irfan Yeşilnacar, M.: Economic performance index assessment of an industrial wastewater treatment plant in terms of the European Green Deal: effect of greenhouse gas emissions. J. Water Climate Change **13**(8), 3100–3118 (2022a)

57. Yapıcıoğlu, P., Yeşilnacar, M.İ: Grey water footprint assessment of groundwater resources in southeastern Turkey: effect of recharge. Water Supply **22**(1), 615–627 (2022b)
58. Yu, J., Wu, Z., An, X., Tian, F., Yu, B.: Trace metal elements mediated co-pyrolysis of biomass and bentonite for the synthesis of biochar with high stability. Sci. Total Environ. **774**, 145611 (2021)
59. Yuan, Y., Bolan, N., Prévoteau, A., Vithanage, M., Biswas, J.K., Ok, Y.S., Wang, H.: Applications of biochar in redox-mediated reactions. Biores. Technol. **246**, 271–281 (2017)
60. Zeghioud, H., Fryda, L., Djelal, H., Assadi, A., Kane, A.: A comprehensive review of biochar in removal of organic pollutants from wastewater: characterization, toxicity, activation/functionalization and influencing treatment factors. J. Water Process Eng. **47**, 102801 (2022)
61. Zhang, Q., Smith, K., Zhao, X., Jin, X., Wang, S., Shen, J., Ren, Z.J.: Greenhouse gas emissions associated with urban water infrastructure: What we have learnt from China's practice. Wiley Interdiscip. Rev. Water **8**(4), e1529 (2021)
62. Zhao, Z., Zhou, W.: Insight into interaction between biochar and soil minerals in changing biochar properties and adsorption capacities for sulfamethoxazole. Environ. Pollut. **245**, 208–217 (2019)
63. Zhao, Y., Liu, Y.: Preparation of hydrogen sulfide adsorbent derived from spent Fenton-like reagent modified biochar and its removal characteristics for hydrogen sulfide. Fuel Process. Technol. **238**, 107495 (2022)
64. Zheng, F., Tan, C., Hou, W., Huang, L., Pan, J., Qi, S.: Does influent COD/N ratio affect nitrogen removal and N2O emission in a novel biochar-sludge amended soil wastewater infiltration system (SWIS)? Water Sci. Technol. **78**(2), 347–357 (2018)
65. Zhou, X., Jia, L., Liang, C., Feng, L., Wang, R., Wu, H.: Simultaneous enhancement of nitrogen removal and nitrous oxide reduction by a saturated biochar-based intermittent aeration vertical flow constructed wetland: effects of influent strength. Chem. Eng. J. **334**, 1842–1850 (2018)
66. Zhou, X., Wang, X., Zhang, H., Wu, H.: Enhanced nitrogen removal of low C/N domestic wastewater using a biochar-amended aerated vertical flow constructed wetland. Biores. Technol. **241**, 269–275 (2017)
67. Zhu, H.L., Papurello, D., Gandiglio, M., Lanzini, A., Akpinar, I., Shearing, P.R., Zhang, Y.S.: Study of H_2S removal capability from simulated biogas by using waste-derived adsorbent materials. Processes **8**(9), 1030 (2020)

Organo-Clay Composites

Surface Modification of Clay with Organics

Marina Massaro, César Viseras-Iborra, and Serena Riela

Abstract Clay minerals are emerging materials which because of their interesting physico-chemical features and morphologies have attracted considerable attention in the last few years. From a chemical point of view, their different chemical compositions allow to modify the clay surface opening the doorway to several strategies to tune the clay's properties. Specifically, it generates nanoarchitectures which have found application in several fields, ranging from biology to industry. Different kind of modification can be envisaged based on the supramolecular interactions of molecules or species with the clay surface or the linkage of specific functionalities. Herein we report the last results in the chemical manipulation of clays surfaces to develop "smart" and multifunctional nanomaterials which have been used as drug carrier and delivery systems, for pollutant removal and as filler for the reinforcement of polymeric matrices. The advantage to modify the clay surfaces over the use of the pristine ones will be also highlighted.

Keywords Clay minerals · Halloysite nanotubes · Hectorite · Supramolecular functionalization · Covalent modification

1 Introduction

The increase in industrialization and urbanization led to an indiscriminate release of pollutants in the surrounding environment. Up to now, environmental pollution is one of the major problem that humanity has to face. Therefore, several efforts have been

---

M. Massaro · S. Riela (✉)
Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF), Università degli Studi di Palermo, 90128 Palermo, Italy
e-mail: serena.riela@unipa.it

C. Viseras-Iborra
Department of Pharmacy and Pharmaceutical Technology, Faculty of Pharmacy, University of Granada, 18071 Granada, Spain

Andalusian Institute of Earth Sciences, CSIC-UGR, 18100 Armilla, Granada, Spain

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_9

made to find the best solutions to removal hazardous materials from the environment. In the years, several systems-based, for example, on silica [1], activated carbon [2], carbon nanotubes [3] and so on, have been used as adsorbent for pollutant, but their high operating costs jeopardize their utilization for a large scale applications. In the first decade of XXI century, it was explored the possibility to use natural clay minerals as sorbent for environmental purposes. The advantages associated to them were soon clear. Indeed, clay minerals are cheaper than other already used systems, and they also provide highly specific surface area.

Clay minerals, formed as products of chemical weathering of other silicate minerals at the earth's surface [4], are natural layer-type phyllosilicate. Depending on the possible arrangements of tetrahedral (T) and octahedral (O) sheets, clay minerals can be classified in different groups the main of which are 1:1 and 2:1. The TO-type structure (1:1) has an octahedral aluminium sheet bonded to a tetrahedral silicon sheet, which belong to this group phyllosilicates such as kaolinite and halloysite. On the contrary, the structure of the TOT type (2:1) consists of an octahedral sheet Al^{3+}, Fe^{3+} or Mg^{2+} sandwiched between two tetrahedral sheets of Si^{4+} or Al^{3+}. In this class of clay minerals belong Hectorite, montmorillonite, and illite are among the clay minerals that belong to this group (Fig. 1).

Because of clay minerals are naturally available and thus are cheap materials, they have been used as raw materials for hundreds of industrial applications such as in construction applications and engineering, food processing, environmental remediation and so on as testified by the increasing number of publications and patents in the last 20 years (Fig. 2).

The use of clay minerals for environmental purposes is renowned since ancient time, the first example, indeed, dates back 5000 years ago, when Greeks and Cypriots

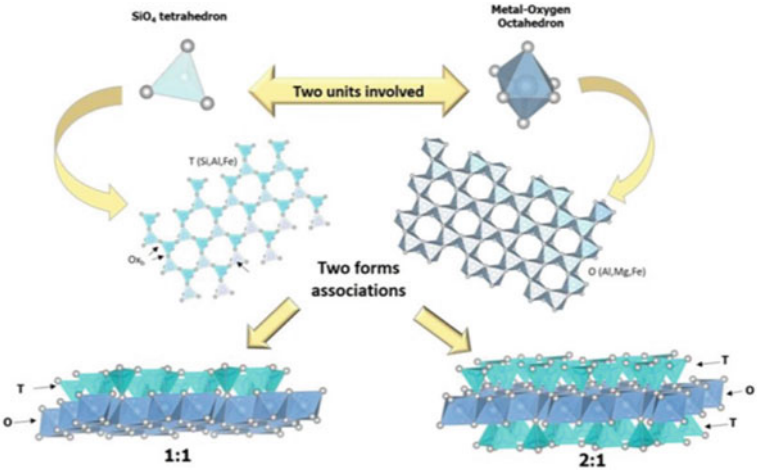


Fig. 1 Representation of tetrahedral and octahedral sheets and 1:1 (TO) and 2:1 (TOT) arrangements in the structure of clay minerals. Reproduced with permission from [5]

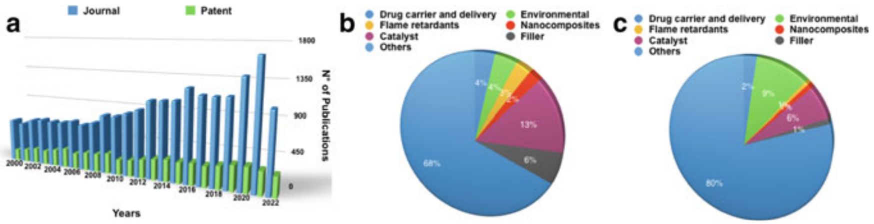


Fig. 2 **a** Distribution (%) of scientific publications in 'patent' and 'journal' for clay minerals; comparison of the number of **b** scientific publications and **c** patents on the different applications fields of clay minerals. Data analysis of publications, as on October 2022, was done using the SciFinder Scholar search system using as 'Document type' the 'Journal' and 'Patent', respectively

usually used clay minerals for bleaching fleece and clothes, and removal of grease and stains form [6]. In the years, owing to their wider natural availability in soils and mine deposits, low cost and biocompatibility, clay minerals have been extensively used as adsorbent materials for several pollutants. Since they possess external surfaces intrinsically negatively charged and hydrophilic and high cation exchange capacity, they show adsorption capabilities towards both cationic and hydrophilic contaminants and inorganic and organic contaminant cations through cation exchange mechanisms.

Among the different clay minerals that can be used for environmental purposes, the most investigated ones are those of kaolin group with a stoichiometry of 1:1, for example halloysite and those with a stoichiometry 2:1, belonging to smectite group such as hectorite.

However, pristine clay minerals often suffer from some limitations due to the fact that, when applied for the adsorption of pollutant, they often don't match the required level of remediation for certain compounds/elements. To solve these problems, several modifications of clay minerals surfaces are envisaged, both supramolecular and covalent [7–10].

In this chapter, we summarize the latest research findings on the modification of halloysite and its combination with hectorite for application in environmental field.

2 Halloysite

Halloysite is a phyllosilicate clay mineral with stoichiometric of 1:1 and a general formula of $Al_2Si_2O_5(OH)_4 \cdot nH_2O$. Naturally, it is mainly found with a nanotubular morphology; thus, it is commonly known as halloysite nanotubes (HNTs). From a geological point of view, the tubes arise from kaolinite by means of the kaolinization process; during this, siloxane groups were placed at the HNTs external surface, whereas the inner one is mainly constituted by a gibbsite-like array of aluminol (Al–OH) groups. Of course, during the rolling process, some defects are created, and they are present at the edge of the tubes as Al–OH and Si–OH groups. Z-potential measurements on an aqueous dispersion of HNTs showed that the nanomaterial

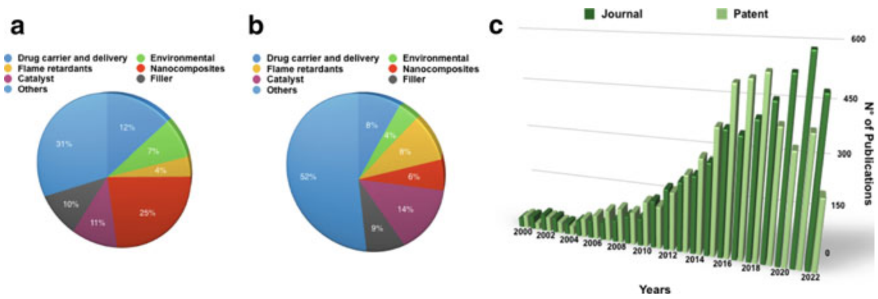


Fig. 3 Comparison of the number of **a** scientific publications and **b** patents on the different applications fields of clay minerals; **c** distribution (%) of scientific publications in 'patent' and 'journal' for halloysite. Data analysis of publications, as on October 2022, was done using the SciFinder Scholar search system using as 'Document type' the 'Journal' and 'Patent', respectively

possesses a negatively charged external surface and a positively charged lumen. All these features make that HNTs can be selectively modified by exploiting different strategies that have allowed the synthesis of different hybrid nanomaterials which can be used as fillers in polymeric matrices [11, 12], biological carriers [13, 14], catalysts [15–17] and so on [18] (Fig. 3a, b). The increasing interest towards this clay is witnessed by the enormous number of publications and patents related to the clay. It is noteworthy that in the last years the number of publications is greater than that of patent, even double in number in 2022, indicating an actual involvement of academia beside the industrial application.

The first documented example of the use of halloysite as adsorbent material for the removal of organic pollutant dates back to 2008, when Zhao and Liu [19] studied the adsorption capacity of the clay towards methylene blue, chosen as cation dye model. In their work, the authors demonstrated that HNTs could efficiently adsorb the dye showing a maximum adsorption capacity of 84.3 $mg \cdot g^{-1}$. These results highlighted the possibility to use the clay for large scale applications. However, as other clay, the use of pristine HNTs for industrial purposes is often hampered by some disadvantages.

Therefore, the functionalization of HNTs is crucial to fully exploit the potentiality of HNTs-based nanomaterials for the utilization in environmental field.

Generally speaking, the functionalization of HNTs surfaces can be based on two different approaches: (i) the supramolecular one and (ii) the covalent modification.

The first one is mainly based on electrostatic attraction and van der Waals interactions, hydrogen bonding and hydrophobic effects. The HNTs lumen indeed is positively charged, and therefore, it can successfully interact with negatively charged or with electron-rich molecules; in addition, it offers a more hydrophobic environment in comparison with surrounding medium which led to the use of the clay as nanocontainer for the loading of different organic molecules. Conversely, the external surface, negatively charged, can interact via electrostatic attraction or hydrogen bonding with positively charged or neutral molecules.

The covalent modification of HNTs external surface exploits the silica chemistry; in particular, it envisages the grafting of organosilanes, via a condensation reaction, between the silanes and the few Si–OH groups of the HNTs present on the edges or on external surface defects [20].

The grafting reactions are carried out in toluene, in water/alcohol mixtures or under solvent-free conditions under MW irradiation. In the years, different organosilanes, bearing different terminal groups, have been used for the HNT modification. Usually, the amount of silane grafted onto the HNTs' surface has been estimated by thermogravimetric analysis measurements. More recently, Licandro et al. reported a new method based on the quantification of Fmoc groups attached to 3-aminopropyltrimethoxysilane (APTES) by UV–vis after their release from the HNTs–APTES–Fmoc system [21].

Table 1 summarizes the different strategies adopted for the modification of HNTs surfaces.

2.1 Metal Ions Removal

The increase in industrialization and urbanization has led to an indiscriminate release of pollutants in the environment. Heavy metal ions are one of the most prevalent harmful species in wastewater and pose a major concern to human health. These, have been classified by US Environmental Protection Agency as dangerous pollutants that due to their no biodegradability and linger, are toxic even at low dose [57]. Therefore, to find adsorbent materials able to remove heavy metal ions from water represents a challenge for scientific community. Halloysite is an emerging inorganic adsorbent material which can be used for this purpose.

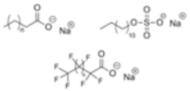
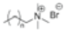
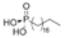
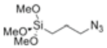
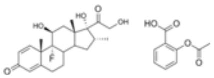
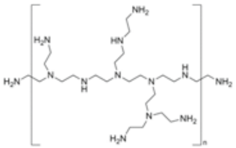
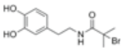
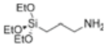
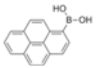
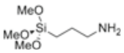
However, the extensive use of HNTs for the removal of metal ions is limited by the occurrence of less metal ion-binding active sites, pristine HNTs low loading capacity and poor selectivity to specific metals [58]. The modification of the surfaces is the most adopted strategy to overcome these limits.

Table 2 reported some HNTs-based nanomaterials used for the removal of heavy metal ions from the environment.

The functionalization of HNTs surface with a positively charged surfactant, hexadecyltrimethylammonium bromide was useful to avoid rapid agglomeration and precipitation of HNTs nanoparticles. The obtained nanomaterial was used by Bing et al. [67] as adsorbent for Cr(IV) removal. It was found that the functionalized HNTs reached an adsorption capacity of 4.3 mg/g (corresponding at ca. 90% of total Cr(IV) removal) after 5 min, reaching 4.4 mg/g (92% removal efficiency) in 10 min. These findings highlighted that the adsorbent showed a rather rapid adsorption rate; thus, a contact time of 30 min is enough for complete adsorption of Cr(VI). In addition, this nanomaterial showed recyclability and reusability for several cycles.

The functionalization of HNTs by the in situ polymerization of pyrrole enables the synthesis of polypyrrole-coated HNTs which showed enhanced ability in Cr(VI) removal [69]. Indeed, in this case, an excellent adsorption capacity of 149.25 mg g^{-1}

Table 1 Overview of the different modification strategies of HNTs surface. Reproduced with permission from [22]

Supramolecular functionalization		Covalent modification	
Inner surface	Outer surface	Inner surface	Outer surface
 Anionic surfactants [23–25]	 Alkyltrimethyl ammonium bromide (cationic surfactants) [26]	 Octadecylposphonic acid [27]	 3-azidopropyltrimethoxysilane [28]
 Dexamethasone [29], aspirin [30] (drugs) [31, 32]	 Poly(ethyleneimine) [33, 34]	 2-bromo-N-[2-(3,4-dihydroxyphenyl)ethyl]-isobutyryl amide [35]	 3-aminopropyltriethoxysilane (APTES) [20, 30, 36]
Lipase, Glucose oxidase, Albumin Laccase and Pepsin (pH < pI) Binase Co-enzymes or enzymes [37–39]	Lipase, Glucose oxidase, Albumin Laccase and Pepsin (pH > pI) Enzymes [39]	 1-pyrenyl boronic acid [40]	 3-aminomethyltrimethoxysilane [41–43]

(continued)

Table 1 (continued)

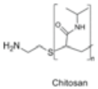
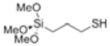
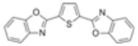
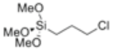
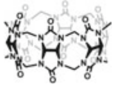
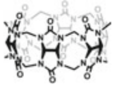
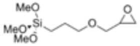
Supramolecular functionalization		Covalent modification	
Inner surface	Outer surface	Inner surface	Outer surface
Pectin Alginate Anionic polymers [44]	 Amine terminated PNIPAAM [45] (cationic polymers) [44]	 1,4-phenylenebisdiboronic acid [46]	 3-mercaptopropyltrimethoxysilane [47, 48]
 Carbon dots [49]	 2,5-bis(2-benzoxazolyl)thiophene [50]	 3-(2-hydroxyethyl)-1-methyl-imidazolium [51]	 3-chloropropyl-trimethoxysilane [52]
 Cucurbituril [53, 54]	 Cucurbituril [53, 54]		 γ-glicidoxypropyltrimethoxysilane [55, 56]

Table 2 HNTs nanomaterials used as adsorbent of heavy metal ions

Nanomaterial	Metal		Reference
HNTs-alginate	Cu(II)	Water	[59]
HNTs modified with polydopamine	Cd(II) and Pb(II)	Water	[60]
HNTs-aniline/Fe_3O_4	Sb(V) and Cr(VI)	Water	[58]
HNTs-NH_2@PVDF	Cr(VI), Cd(II) and Cu(II)	Water	[61]
Alkaline activated HNTs	Several metals	Water	[62]
HNTs, pristine, calcined and acid-activated	Cd(II), Pb(II), As(V), and Zn(II)	Water	[63]
HNTs/chitosan/spirulina	Cr(VI)		[64]
HNTs-SH or HNTs-NH_2	Cu, Cd, Zn, As, Pb	Soil	[65]
HNTs/diethanolamine/ triethanolamine	Zn(II), Cd(II), Pb(II), and Cu(II)	Water	[66]
HNTs/hexadecyltrimethylammonium bromide	Cr(VI)	Water	[67]
HNTs/alginate	Pb(II)	Water	[68]

at pH 2.0 was observed. The nanomaterial also was recyclable for at least three cycles without loss of its original removal efficiency. The most important aspect of this work was due to the fact that the authors tested the adsorption capacity of the nanocomposite on Cr(VI) contaminated chrome mine wastewater and groundwater and the results highlighted the feasibility of the material to be applied as adsorbent for the remediation of Cr(VI).

The covalent modification of HNTs external surface with organosilanes bearing amino groups led to synthesis of a series of nanomaterials which showed enhanced adsorption abilities towards metal ions, owing to the high affinity between the latter and amino groups. The amino-modified HNTs were used as they are or as filler for filtration membranes. For example, He et al. reported the incorporation of different concentration of HNTs-NH_2 into polyvinylidene fluoride (PVDF) nanofiltration membranes and the obtained nanocomposite was tested as adsorbent for Cu(II), Cr(IV) and Cd(II) ions from simulated wastewater (Fig. 4). The results showed that the amount of metal ions removed depended from the concentration of modified HNTs into the membrane and that, due to the presence of HNTs, blend membrane had better anti-pollution and reuse performances compared with PVDF membrane [61].

In another work, HNTs-NH_2 were used as adsorbent for the removal of Pb^{2+} ions. The experimental results showed that the introduction of amino functionalities onto HNTs external surface was crucial in the increasing of adsorption rate and that the adsorption efficiency is better by increasing the pH and decreasing the ionic strength of the medium, in comparison with data obtained in the presence of pristine HNTs at the same experimental conditions (Fig. 5) [70].

Going further, several organosilanes bearing amino groups were used to improve the adsorption performances of the HNTs-based materials. For example, N-β-Aminoethyl-γ-aminopropyl trimethoxysilane was used to modify HNTs external

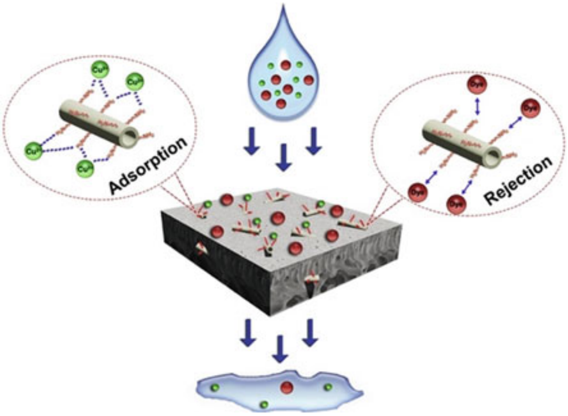


Fig. 4 Nanofiltration membrane based on amino-modified HNTs and PVDF for metal ions removal. Reproduced with permission from [61]

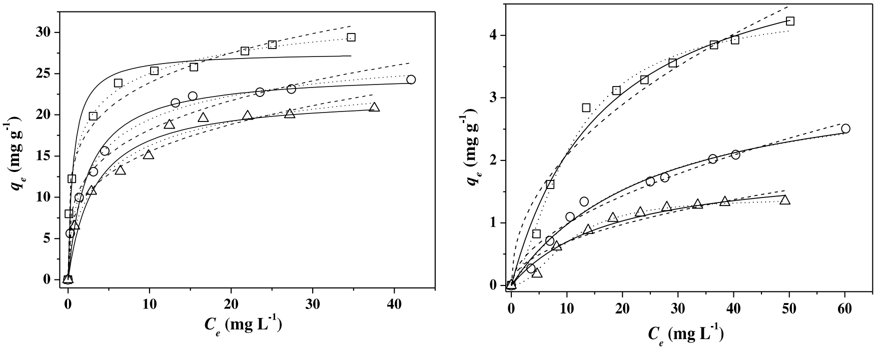


Fig. 5 Adsorption isotherms of Pb(II) ions on **a** HNTs-NH_2 and **b** pristine HNTs from aqueous solutions at pH = 5.0 containing NaCl 0.10 (squares), 0.25 (circles), 0.50 (triangles) mol L^{-1} and at T = 25 °C. Experimental data fitted with Freundlich (dashed lines), Langmuir (continuous lines) and Sips (dotted lines) models. Reproduced with permission from [70]

surface to develop a sorbent material with enhanced performance in Cr(VI) removal from wastewater [71]. The experimental findings highlighted that electrostatic interaction between Cr(VI) ions and adsorbents is crucial in the adsorption process.

Based on these considerations, Wang et al. varied the terminal groups onto the silane to obtain different HNTs-based nanomaterials which can interact in different way with the metals [58]. The adsorption efficiency was tested for the simultaneously removal of Sb(V) and Cr(VI) ions from simulated wastewater. The used silanes are depicted in Fig. 6.

It was found that the HNTs modified with the KH-42 showed, among the investigated nanomaterials, the highest removal efficiency towards Cr(VI) which can be attributed to the interactions between $HCrO_4^-$ and aromatic compounds on

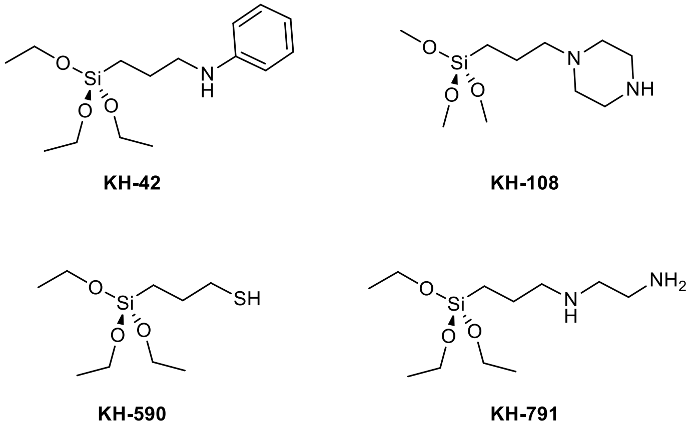


Fig. 6 Silanes used for the functionalization of HNTs for environmental purposes. Reproduced with permission from [72]

HNTs, forming anion-π complexes. Conversely, KH-108-modified HNTs showed the highest removal efficiency for Sb(V) at acidic conditions, which might be due to the interaction between negatively charged $Sb(OH)_6^-$ and the positively charged amino functional groups present in acidic environment.

Amino and thiol-modified HNTs were successfully used for the removal of Hg(II) ions [73]. The authors of this study demonstrated that the introduction of the organic groups increases the adsorption capacity of pristine HNTs in a pH range of 3–5 and besides the pH, the factors which influence the adsorption are the ionic medium, and the ionic strength of aqueous solution. By mechanistic considerations, it is possible to conclude that modified HNTs remove the Hg(II) ions by a physical adsorption mechanism enhanced by ion exchange.

These results demonstrated that by the modification of HNTs, not only improves the adsorption properties in comparison to the pristine clay, but also it is possible to remove selectively a metal ion over another. For example, the introduction of acrylonitrile onto HNTs, by the modification of their surface with vinyltriethoxysilane [74], serves as scaffold to synthetize an amidoxime group which was selective for uranium adsorption. The experimental results highlighted an adsorption capacity of 456.24 mg g^{-1} in 32 ppm uranium-spiked simulated seawater with a saturation time of 13 h. In natural seawater, the material reached the uranium extraction capacity of 5.70 mg g^{-1} and 9.01 mg g^{-1} after a field test of 5 days and 30 days, respectively.

The post-modification of HNTs-NH_2 nanomaterial with the coumarin derivative (7-hydroxy-2-ox-2H-chromene-5-carbaldehyde) was useful for Zn(II) ion removal. This nanomaterial indeed showed a selectively turn-on fluorescence response in the presence of the metal ions.

Similarly, PAMAM units bearing terminal alkyne were linked onto the external surface of thiol modified HNTs by a thiol-yne click reaction [75] affording a nanomaterial which showed an high affinity for Pb(II) ions. The adsorption studies demonstrated that the synthetized nanomaterial possesses a high adsorption capacity of 194.4 mg g^{-1}. Recyclability studies showed that it is highly recyclable possessing 90% of the maximum adsorption capacity after six consecutive runs.

These examples showed that by the suitable choose of the starting organosilanes, it is possible to obtain nanomaterials with tunable surface to improve the utilization of HNTs in heavy metal ions removal.

2.2 Organic Pollutants

According to the Convention of Stockholm, another class of persistent pollutants in wastewater is represented by the so-called Persistent Organic Pollutant [76]. These are mainly carbon-based molecules, such as dyestuffs, solvents, industrial chemical by-products (polycyclic aromatic hydrocarbons, dioxins, perfluorinated compounds) and pesticides [77, 78] that are released in the environment from different sources, and therefore, their removal is of fundamental importance. Currently, several methods are employed to treat the wastewater in order to reduce the presence of contaminants [79]. Some of them are based on the use of modified halloysite as adsorbent materials, catalysts for photodegradation or reduction of organic molecules.

2.2.1 Adsorption

By the physisorption of Fe_3O_4 nanoparticles onto HNTs external surface, Ma et al. [80] developed a magnetic nanomaterial that was used as inorganic sorbent for methylene blue and Nile Red, chosen as models for cationic dyes, and methyl orange, as the anionic one. Due to the different HNTs charged surfaces, the nanomaterial was selective for cationic dyes that were successfully on the negatively charged external surface, whereas poor adsorption towards the anionic methyl orange was observed. The functionalization of the surface with magnetic nanoparticles, allowed easier recyclability than the pristine HNTs.

By exploiting an electrostatic self-assembly process Liu, Zhang et al. reported the loading of HNTs on the surface of reduced graphene oxide sheets [81] to obtain a nanosystem that, after its modification with APTES, showed promising adsorption capacities towards Rhodamine B.

A magnetic nanomaterial based on HNTs was fabricated by the modification of the clay surface with carboxylic groups. The nanomaterial was then used as support for the synthesis of molecular imprinted polymers which material showed a fast and selective recognition of 2,4,6-trichlorophenol from aqueous solutions [82].

The introduction of HNTs as filler in polydopamine matrix allowed to obtain two different nanomaterials, which showed, depending on the synthetic pathway, promising adsorption capability for the development of membrane coating for Rhodamine B removal [83].

Cyclodextrin units were linked on thiol modified HNTs, by a thiol-ene reaction in the presence of AIBN, under MW irradiation in solvent-free conditions [84]. By adopting this strategy, it was possible to obtain a hyper-reticulated system, similar to a nanosponge, which possesses two different cavities useful for organic dyes adsorption. Adsorption studies and kinetic experiments showed the existence of different interaction sites and high adsorption efficiencies towards Rhodamine B. In addition, by expanding the scope of the nanomaterial, it was demonstrated a selectivity in the removal cationic dyes in comparison to the anionic ones.

The supramolecular functionalization of both HNTs with cucurbit[8]uril molecules [54] was a useful strategy to synthetize used as nanosponges for the capture of aromatic compounds. Due to the high hydrophobicity of the system, indeed, it was possible to remove pyrene from aqueous systems and toluene molecules from both liquid and gas phases. In the latter case, the nanosponges showed a high performance in capturing toluene gas with respect to the pristine HNTs. The adsorbed amount of toluene, indeed, is larger for the nanosponges in all contact times investigated; for example, after 2 h, the toluene amount captured by the nanosponge is ca. 50 times larger than that of pristine HNTs.

2.2.2 Photodegradation

Supporting metal nanoparticles onto HNTs is a strategy common adopted to synthetize valuable photocatalysts which have been used for environmental purposes [85–91]. Some of them are reported in Table 3.

As it is possible to note from Table 3, the most used nanoparticles are the TiO_2 ones which were supported on HNTs showing promising photocatalytic activity.

An electrospun carbon doped TiO_2/HNTs nanofiber was proposed by Liu et al. [94] to generate a photocatalyst for the degradation of organic dyes. The experimental findings highlighted that the visible light photocatalytic efficiency of the nanofiber was enhanced by a HNTs doping amount of ca. 8%, greater than that of commercial anatase TiO_2.

Recently, to improve their photocatalytic properties, Lee et al. synthetized a La^{3+} doped TiO_2 on HNTs (La/TiO_2@HNTs) nanomaterial [100] by a multi-step procedure (Fig. 7) to achieve a synergistic photolysis activity enhancement. The combination of HNTs and lanthanum doping on TiO_2, indeed, increased the catalytic activity of the nanoparticles by ca. 3 times with respect to undoped TiO_2. The use of HNTs as support also ensures recyclability by offering an easy separation method using centrifugation.

The complexation of EDTA inside the HNTs lumen was helpful in the immobilization of α-Fe_2O_3 because of the strong affinity of EDTA for Fe^{3+} ions [101]. The nanomaterial so obtained showed enhanced photocatalytic activity towards organic dyes under UV, *vis* and direct sunlight irradiation at room temperature with respect to pristine HNTs.

Table 3 Metal nanoparticles supported on HNTs for application as photocatalysts for pollutant removal

Metal NPs	Pollutant	Reference
TiO_2	RhB	[89]
CdS	Tetracycline	[86]
ZnO	Tetracycline	[88]
AgNPs	MB	[87]
CeO_2/AgBr	MO	[85]
Au-Ni/Fe_3O_4	Congo Red	[90]
TiO_2	MB	[92–94]
ZnO or TiO_2	MB	[95]
$LaFeO_3$	Chlortetracycline	[96]
TiO_2 and Fe_2O_3	2-chloro-, 2,6-dichloroaniline and aniline	[97]
$W_{18}O_{49}$	MO	[98]
Fe_3O_4	MB	[99]

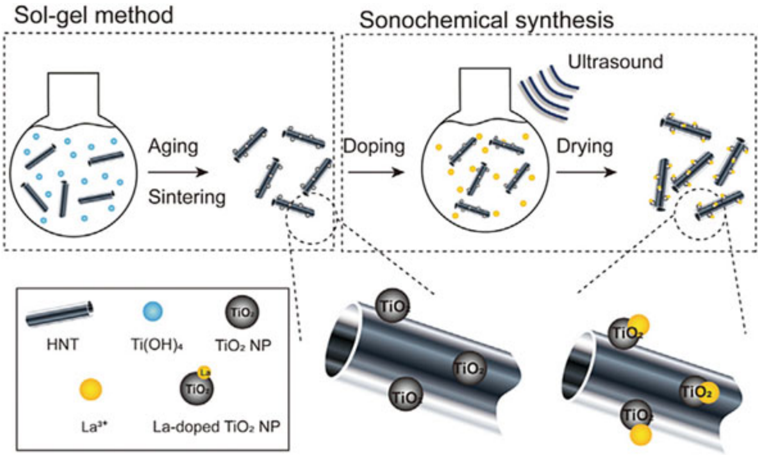


Fig. 7 Synthesis of La/TiO_2@HNTs nanomaterial. Reproduced with permission from [100]

Commercial bulk ZnO were immobilized onto HNTs in a phosphate buffer pH 8.0 affording the HNT@ZnO nanomaterial [102]. It was very efficient for the photodegradation of methyl orange and Rhodamine B under UV light. The authors of the work also demonstrated, by mechanistic studied and trapping experiments that the main species responsible for the photodegradation of the dyes are•OH radicals produced during the process.

2.2.3 Reduction Reactions

The loading of Ag nanoparticles (AgNPs) into HNTs lumen by electrostatic interactions by negatively charged N-acetyl-L-cysteine-modified AgNPs [103] and the positively charged HNTs lumen led to the development of an innovative system with good catalytic performance and reusability for 4-nitrophenol reduction. Similarly, the immobilization of Co_3O_4 nanoparticles onto HNTs by a non-aqueous deposition–precipitation, followed by thermal treatment, was found to be a successful strategy to obtain an efficient nanomaterial for the reduction of 4-nitrophenol and organic dyes [104].

Catalytic studies showed that the Co_3O_4/HNTs nanomaterial displayed enhanced performances towards the reduction of aqueous organic contaminants in terms of durability, conversion rate, and induction period with respect to the unsupported Co_3O_4 nanoparticles. These promising results were explained by an influence of HNTs as support which endowed Co_3O_4 nanoparticle with the cooperative effects and the specific structural characteristics.

Modification of HNTs external surface with thiol groups was useful for the immobilization of AuNPs, by exploiting the strong gold-thiol affinity [105]. The so-obtained nanomaterial demonstrated to be highly active in the reduction of 4-nitrophenol showing remarkable TOF values (up to 2 204 530 h^{-1}).

Besides the functionalization approaches described above, other strategies have been adopted to increase the adsorption efficiency of HNTs towards different pollutants. For example, it is possible to intercalate small molecules into halloysite interlayer. In this context, Khelifa et al. reported the intercalation of sodium acetate into HNTs [106]. This strategy allowed the authors to an increase of HNTs' adsorption properties towards metal ions. In particular, they demonstrated high efficiency in the Cu(II) ions adsorption and that the intercalated HNTs retained the loaded Cu(II) metal 2.2 times larger than pristine clay.

Furthermore, chemical manipulation of HNTs surfaces by the treatment with strong acid or base helps in the development of systems which showed, in comparison with pristine HNTs, enhanced adsorption capacities. For example, acid-treated HNTs were employed to remove a series of chloroanilines, namely 3-,4-chloroaniline and 3,4 dichloroaniline [107]. By using different acid concentrations, ranging from 20 to 65 mass%, it was found that the modified HNTs showed the best adsorption capacity when treated with 50% sulphuric acid.

2.3 Carriers for Pesticides

When the environment is concerned, it has to be faced another problem deriving from the extensive use of pesticides. The growth of population required more and more food production which is hampered by the climate changes, and agricultural crop pests, to mention some of them. These lead to an indiscriminate introduction of pesticides in the environment that contaminate soil, water and even food.

The development of systems capable to carrier and gradually release the pesticides is crucial to reduce their environmental impact. In this context halloysite, which has shown excellent eco-compatibility, [108–110] represents an inexpensive carrier for several pesticides.

Acid treated HNTs were used as carrier for chlorpyrifos (CPF), a hydrophobic pesticide, followed by the coating of the tubes with alginate gels, used to slow down the release of the CPF from the tubes. To increase the loading of the active ingredient, a three-dimensional structure involving the acid-treated HNTs was also created via a step-by-step modification of the HNTs surface with Ca^{2+} and $EDTA^{2-}$ exploiting their strong coordination interactions (Fig. 8) [111].

In addition, the obtained system showed an increase of ca. 86%, in comparison with pristine CPF, of foliar adhesion property against rain rinsing, probably because of the strong interactions which exist between alginate and plant leaves.

A similar strategy was used for the development of a novel pesticide based on CPF to fight the growth of beet armyworm (which grows fastest at 35 °C) [112]. In this case, HNTs were covalently modified by a thermo-responsive polymer, the poly-isopropylacrylamide (PNIPAAM), and the obtained nanomaterial was further coated with polydopamine in an attempt to slow down the CPF release. The use of the thermoresponsive PNIPAAM was crucial since the final nanomaterial showed a release rate, of the active specie, ca. 2.5 times higher at 35 °C than that at 25 °C.

A xylene solution of chlorantraniliprole (CAP) was mixed with an aqueous dispersion of HNTs affording a three-dimensional network structure that showed important properties for application in agriculture. Indeed, the CAP in the nanocomposite possessed enhanced leaf adhesion, rain erosion resistance and insecticidal effect with respect to “free” CAP [113]. Promising insecticidal activity was showed by in vivo test on *S. frugiperda*, selected as pest model.

The advantage to use HNTs for agricultural purposes relies also in the possibility to develop nanosystems for pesticides preservation. In this context, for example, the loading of pyrethrum extract into HNTs lumen allowed the protection of the active species from UV light and avoided the hydrolysis in aqueous media the pyrethrins,

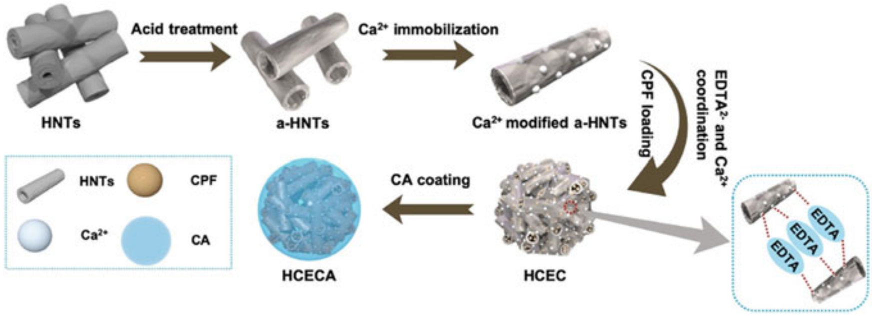


Fig. 8 Schematic representation of the HNTs/CPF pesticide. Reproduced with permission from [111]

main components of the natural extract. These advantages translate into an enhanced pesticidal activity. In vivo tests on *G. mellonella*, chosen as pest model, indeed showed that the nanomaterial was highly active even at half dose respect to the recommended field dose [114].

2.4 Combination of Clays for Environmental Purposes: Covalent Modification of HNTs with Hectorite

Recently, to fully exploit the feasibility of HNTs as adsorbent material for several hazardous species, beside the modification of their surfaces or the chemical manipulation, it has been proposed the combination with other clays. In particular, from an experimental point of view, it results advantageous the covalent linkage between HNTs with another clay with complementary adsorption capability such as hectorite.

Hectorite (Ht) is a clay mineral belonging to the smectite group, with an ideal chemical formula of $Na_{0.3}Mg_{2.7}Li_{0.3}Si_4O_{10}(OH)_2$. Chemically, it is constituted by different layers of Si–O–Mg(Li)–O–Si–with hydrated cations (e.g. Na^+, Li^+) in the interlayer space. Similar to other clays, Ht nanolayers showed different charged surfaces, in particular it is negative on the basal faces (composed of Si–O–Si groups) and pH-dependent charge on the edges [115]. Furthermore, the Si–O–Si groups confer hydrophobic properties to the basal faces, while the Si–OH groups present at the edges can be chemically modified [116, 117], by a similar approach used for HNTs external surface. The advantage to use Ht for environmental purposes relies in its high cation exchange capacity (CEC) that is in the range from 50 to 150 mmol/100 g in a pH range from 6 to 13 [118], and specific surface area about 350 $m^2\ g^{-1}$ [119].

When it is used as adsorbent material, the main forces involved in the adsorption process are based on electrostatic attractions, surface complexation, Van der Waals force and ion exchange between adsorbates and the surface of hectorite [115]. The modification of the edge with organics, of course increases the adsorption selectivity and capacity towards heavy metal ions. As example, the modification of the Ht edges by grafting 2-(3-(2-aminoethylthio)propylthio)ethanamine allowed to obtain a good nanoadsorbent for the removal of Hg(II) and Ag(I) ions from aqueous environment [120]. Supramolecular functionalization of Ht with cetylpyridinium bromide gave a nanomaterial which possessed enhanced adsorption capability towards Neutral Red in comparison with the pristine clay [121].

From these premises, it is clear that the combination of Ht and HNTs could be beneficial in improving HNTs properties by the design and development of nanoarchitectures which could benefit, in terms of thermal stability, adsorption abilities, solvent resistance and so on, of both Ht and HNTs properties.

The covalent linkage between the two clays was achieved by a multi-step procedure where the both pristine clays were firstly modified with suitable organosilanes bearing complementary terminal groups. In particular, HNTs external surface was modified by 3-mercaptopropyltrimethoxy silane, whereas the Ht edges were reacted with 3-aminoprópryltrimethoxy silane followed by a nucleophilic substitution with allyl bromide to introduce allyl groups at Ht edges [122].

Afterwards, the two clays were linked by a thiol-ene reaction mediated by AIBN under MW irradiation in solvent-free conditions. The covalent linkage was verified by several techniques, and by morphological investigations by S/TEM analysis, it was highlighted that the morphology of the nanomaterial obtained is coherent with the combination of the two clays, indeed, it was found the HNTs results covered by Ht (Fig. 9), conversely to the physical mixture which shows the two clays randomly dispersed.

The nanomaterial showed promising adsorption ability to simultaneously remove both ciprofloxacin (chosen as antibiotic model) and Ag^+ ions. The experimental results showed that the nanomaterial can adsorb ca. 2.6 wt% of ciprofloxacin and ca. 8 wt% of Ag^+ ions, as estimated by thermogravimetric analysis and AgCl test, respectively.

3 Conclusions

Clay minerals were used as adsorbent materials from ancient time. Among them, halloysite nanotubes, because of their interesting physico-chemical properties are among the most studied ones for environmental purposes. Their modification both by supramolecular and covalent approaches improves their adsorption capabilities towards heavy metal ions and organic hazardous molecules in comparison with the pristine HNTs. Furthermore, their covalent combination with other clays, with complementary adsorption capability, such as hectorite, allowed to obtain innovative nanoadsorbent to simultaneous remove from wastewater different pollutant.

Therefore, the introduction of organic functionalities onto the clays surface represent a valuable strategy to obtain cheap and efficient nanoadsorbent for environmental purposes.

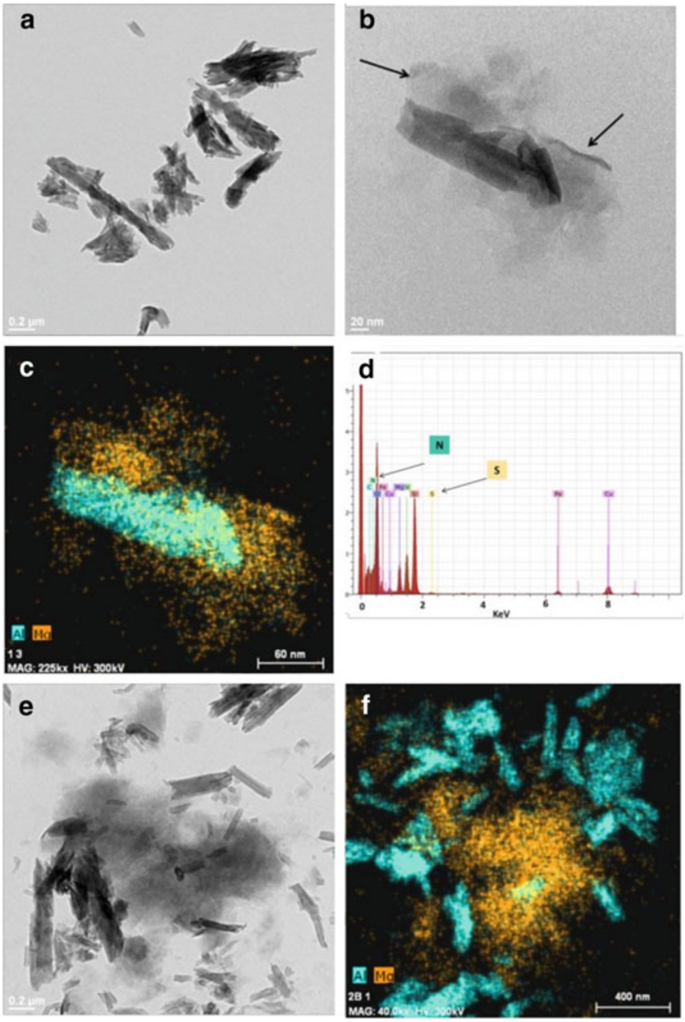


Fig. 9 **a**, **b** TEM image of HNTs-Ht nanomaterial (scale bar 200 and 20 nm, respectively); **c** corresponding EDX image of Al and Mg from STEM image (scale bar 60 nm); **d** EDX spectrum of the HNTs-Ht nanomaterial; **e** TEM image of the physical mixture constituted by HNTs and Ht (scale bar 0.2 μm); and **f** the corresponding EDX image of Al and Mg from STEM image (scale bar 0.4 μm). Reproduced with permission from [122]

References

1. Parida, S.K., Dash, S., Patel, S., Mishra, B.K.: Adsorption of organic molecules on silica surface. Adv. Colloid Interface Sci. **121**(1), 77–110 (2006). https://doi.org/10.1016/j.cis.2006.05.028
2. Pereira, M.F.R., Soares, S.F., Órfão, J.J.M., Figueiredo, J.L.: Adsorption of dyes on activated carbons: influence of surface chemical groups. Carbon **41**(4), 811–821 (2003). https://doi.org/10.1016/S0008-6223(02)00406-2
3. Yan, Y., Zhang, M., Gong, K., Su, L., Guo, Z., Mao, L.: Adsorption of methylene blue dye onto carbon nanotubes: a route to an electrochemically functional nanostructure and its layer-by-layer assembled nanocomposite. Chem. Mater. **17**(13), 3457–3463 (2005). https://doi.org/10.1021/cm0504182
4. Sposito, G., Skipper, N.T., Sutton, R., Park, S.-H., Soper, A.K., Greathouse, J.A.: Surface geochemistry of the clay minerals. Proc. Natl. Acad. Sci. **96**(7), 3358–3364 (1999). https://doi.org/10.1073/pnas.96.7.3358
5. da Rocha, M.C., Galdino, T., Trigueiro, P., Honorio, L.M.C., de Melo Barbosa, R., Carrasco, S.M., Silva-Filho, E.C., Osajima, J.A., Viseras, C.: Clays as vehicles for drug photostability. Pharmaceutics **14**(4), 796 (2022)
6. Rytwo, G.: Clay minerals as an ancient nanotechnology: historical uses of clay organic interactions, and future possible perspectives. In: 2008
7. Shabtai, I.A., Mishael, Y.G.: Catalytic polymer-clay composite for enhanced removal and degradation of diazinon. J. Hazard. Mater. **335**, 135–142 (2017). https://doi.org/10.1016/j.jhazmat.2017.04.017
8. Shabtai, I.A., Mishael, Y.G.: Polycyclodextrin-clay composites: Regenerable dual-site sorbents for bisphenol A removal from treated wastewater. ACS Appl. Mater. Interfaces **10**(32), 27088–27097 (2018). https://doi.org/10.1021/acsami.8b09715
9. Ray, J.R., Shabtai, I.A., Teixidó, M., Mishael, Y.G., Sedlak, D.L.: Polymer-clay composite geomedia for sorptive removal of trace organic compounds and metals in urban stormwater. Water Res. **157**, 454–462 (2019). https://doi.org/10.1016/j.watres.2019.03.097
10. Osovsky, R., Cherf, S., Karagach, S., Aviram, L., Mishael, Y.: Decontamination of sarin in water by designed oxime-clay composites. Appl. Clay Sci. **192**, 105620 (2020). https://doi.org/10.1016/j.clay.2020.105620
11. Ye, J.J., Li, L.F., Hao, R.N., Gong, M., Wang, T., Song, J., Meng, Q.H., Zhao, N.N., Xu, F.J., Lvov, Y., Zhang, L.Q., Xue, J.J.: Phase-change composite filled natural nanotubes in hydrogel promote wound healing under photothermally triggered drug release. Bioact. Mater. **21**, 284–298 (2023). https://doi.org/10.1016/j.bioactmat.2022.08.026
12. Zhao, P., Feng, Y., Zhou, Y., Tan, C., Liu, M.: Gold@Halloysite nanotubes-chitin composite hydrogel with antibacterial and hemostatic activity for wound healing. Bioact. Mater. **20**, 355–367 (2023). https://doi.org/10.1016/j.bioactmat.2022.05.035
13. Massaro, M., Buscemi, G., Arista, L., Biddeci, G., Cavallaro, G., D’Anna, F., Di Blasi, F., Ferrante, A., Lazzara, G., Rizzo, C., Spinelli, G., Ullrich, T., Riela, S.: Multifunctional carrier based on halloysite/laponite hybrid hydrogel for kartogenin delivery. ACS Med. Chem. Lett. **10**(4), 419–424 (2019). https://doi.org/10.1021/acsmedchemlett.8b00465
14. Massaro, M., Licandro, E., Cauteruccio, S., Lazzara, G., Liotta, L.F., Notarbartolo, M., Raymo, F.M., Sánchez-Espejo, R., Viseras-Iborra, C., Riela, S.: Nanocarrier based on halloysite and fluorescent probe for intracellular delivery of peptide nucleic acids. J. Colloid Interface Sci. **620**, 221–233 (2022). https://doi.org/10.1016/j.jcis.2022.03.151
15. Stavitskaya, A.V., Kozlova, E.A., Kurenkova, A.Y., Glotov, A.P., Selischev, D.S., Ivanov, E.V., Kozlov, D.V., Vinokurov, V.A., Fakhrullin, R.F., Lvov, Y.M.: Ru/CdS quantum dots templated on clay nanotubes as visible-light-active photocatalysts: optimization of S/Cd ratio and Ru content. Chem. – Eur. J. **26**(57), 13085–13092 (2020). https://doi.org/10.1002/chem.202002192

16. Stavitskaya, A., Mazurova, K., Kotelev, M., Eliseev, O., Gushchin, P., Glotov, A., Kazantsev, R., Vinokurov, V., Lvov, Y.: Ruthenium-loaded halloysite nanotubes as mesocatalysts for Fischer-Tropsch synthesis. Molecules **25**(8), 1764 (2020)
17. Stavitskaya, A., Glotov, A., Pouresmaeil, F., Potapenko, K., Sitmukhanova, E., Mazurova, K., Ivanov, E., Kozlova, E., Vinokurov, V., Lvov, Y.: CdS quantum dots in hierarchical mesoporous silica templated on clay nanotubes: implications for photocatalytic hydrogen production. ACS Appl. Nano Mater. **5**(1), 605–614 (2022). https://doi.org/10.1021/acsanm.1c03393
18. Stavitskaya, A., Rubtsova, M., Glotov, A., Vinokurov, V., Vutolkina, A., Fakhrullin, R., Lvov, Y.: Architectural design of core–shell nanotube systems based on aluminosilicate clay. Nanoscale Adv. **4**(13), 2823–2835 (2022). https://doi.org/10.1039/D2NA00163B
19. Zhao, M., Liu, P.: Adsorption behavior of methylene blue on halloysite nanotubes. Microporous Mesoporous Mater. **112**(1), 419–424 (2008). https://doi.org/10.1016/j.micromeso.2007.10.018
20. Yuan, P., Southon, P.D., Liu, Z., Green, M.E.R., Hook, J.M., Antill, S.J., Kepert, C.J.: Functionalization of halloysite clay nanotubes by grafting with γ-aminopropyltriethoxysilane. J. Phys. Chem. C **112**(40), 15742–15751 (2008). https://doi.org/10.1021/jp805657t
21. Fidecka, K., Giacoboni, J., Picconi, P., Vago, R., Licandro, E.: Quantification of amino groups on halloysite surfaces using the Fmoc-method. RSC Adv. **10**(24), 13944–13948 (2020). https://doi.org/10.1039/D0RA01994A
22. Massaro, M., Cavallaro, G., Colletti, C.G., Lazzara, G., Milioto, S., Noto, R., Riela, S.: Chemical modification of halloysite nanotubes for controlled loading and release. J. Mater. Chem. B **6**(21), 3415–3433 (2018). https://doi.org/10.1039/C8TB00543E
23. Cavallaro, G., Lazzara, G., Milioto, S.: Exploiting the colloidal stability and solubilization ability of clay nanotubes/ionic surfactant hybrid nanomaterials. J. Phys. Chem. C **116**(41), 21932–21938 (2012). https://doi.org/10.1021/jp307961q
24. Cavallaro, G., Lazzara, G., Milioto, S., Palmisano, G., Parisi, F.: Halloysite nanotube with fluorinated lumen: non-foaming nanocontainer for storage and controlled release of oxygen in aqueous media. J. Colloid Interface Sci. **417**, 66–71 (2014). https://doi.org/10.1016/j.jcis.2013.11.026
25. Cavallaro, G., Lazzara, G., Milioto, S., Parisi, F., Sanzillo, V.: Modified halloysite nanotubes: nanoarchitectures for enhancing the capture of oils from vapor and liquid phases. ACS Appl. Mater. Interfaces **6**(1), 606–612 (2014). https://doi.org/10.1021/am404693r
26. Cavallaro, G., Lazzara, G., Milioto, S., Parisi, F.: Hydrophobically modified halloysite nanotubes as reverse micelles for water-in-oil emulsion. Langmuir **31**(27), 7472–7478 (2015). https://doi.org/10.1021/acs.langmuir.5b01181
27. Yah, W.O., Takahara, A., Lvov, Y.M.: Selective modification of halloysite lumen with octadecylphosphonic acid: new inorganic tubular micelle. J. Am. Chem. Soc. **134**(3), 1853–1859 (2012). https://doi.org/10.1021/ja210258y
28. Riela, S., Massaro, M., Colletti, C.G., Bommarito, A., Giordano, C., Milioto, S., Noto, R., Poma, P., Lazzara, G.: Development and characterization of co-loaded curcumin/triazole-halloysite systems and evaluation of their potential anticancer activity. Int. J. Pharm. **475**(1–2), 613–623 (2014). https://doi.org/10.1016/j.ijpharm.2014.09.019
29. Veerabadran, N.G., Mongayt, D., Torchilin, V., Price, R.R., Lvov, Y.M.: Organized shells on clay nanotubes for controlled release of macromolecules. Macromol. Rapid Commun. **30**(2), 99–103 (2009). https://doi.org/10.1002/marc.200800510
30. Lun, H., Ouyang, J., Yang, H.: Natural halloysite nanotubes modified as an aspirin carrier. RSC Adv. **4**(83), 44197–44202 (2014). https://doi.org/10.1039/C4RA09006C
31. Yendluri, R., Lvov, Y., de Villiers, M.M., Vinokurov, V., Naumenko, E., Tarasova, E., Fakhrullin, R.: Paclitaxel encapsulated in halloysite clay nanotubes for intestinal and intracellular delivery. J. Pharm. Sci. **106**(10), 3131–3139 (2017). https://doi.org/10.1016/j.xphs.2017.05.034
32. Yendluri, R., Otto, D.P., De Villiers, M.M., Vinokurov, V., Lvov, Y.M.: Application of halloysite clay nanotubes as a pharmaceutical excipient. Int. J. Pharm. **521**(1), 267–273 (2017). https://doi.org/10.1016/j.ijpharm.2017.02.055

33. Lvov, Y., Price, R., Gaber, B., Ichinose, I.: Thin film nanofabrication via layer-by-layer adsorption of tubule halloysite, spherical silica, proteins and polycations. Colloids Surf., A **198–200**, 375–382 (2002). https://doi.org/10.1016/S0927-7757(01)00970-0
34. Kim, J., Park, N.-H., Na, J.H., Han, J.: Development of natural insect-repellent loaded halloysite nanotubes and their application to food packaging to prevent Plodia interpunctella infestation. J. Food Sci. **81**(8), E1956–E1965 (2016). https://doi.org/10.1111/1750-3841.13373
35. Yah, W.O., Xu, H., Soejima, H., Ma, W., Lvov, Y., Takahara, A.: Biomimetic dopamine derivative for selective polymer modification of halloysite nanotube lumen. J. Am. Chem. Soc. **134**(29), 12134–12137 (2012). https://doi.org/10.1021/ja303340f
36. Tan, D., Yuan, P., Annabi-Bergaya, F., Liu, D., Wang, L., Liu, H., He, H.: Loading and in vitro release of ibuprofen in tubular halloysite. Appl. Clay Sci. **96**, 50–55 (2014). https://doi.org/10.1016/j.clay.2014.01.018
37. Price, R., Gaber, B.P., Lvov, Y., Price, R.: In-vitro release characteristics of tetracycline HCl, khellin and nicotinamide adenine dineculeotide from halloysite; a cylindrical mineral. J. Microencapsul. **18**(6), 713–722 (2001). https://doi.org/10.1080/02652040010019532
38. Sun, J., Yendluri, R., Liu, K., Guo, Y., Lvov, Y., Yan, X.: Enzyme-immobilized clay nanotube-chitosan membranes with sustainable biocatalytic activities. PCCP **19**(1), 562–567 (2017). https://doi.org/10.1039/C6CP07450B
39. Tully, J., Yendluri, R., Lvov, Y.: Halloysite clay nanotubes for enzyme immobilization. Biomacromol **17**(2), 615–621 (2016). https://doi.org/10.1021/acs.biomac.5b01542
40. Zhang, H., Ren, T., Ji, Y., Han, L., Wu, Y., Song, H., Bai, L., Ba, X.: Selective modification of halloysite nanotubes with 1-pyrenylboronic acid: a novel fluorescence probe with highly selective and sensitive response to hyperoxide. ACS Appl. Mater. Interfaces **7**(42), 23805–23811 (2015). https://doi.org/10.1021/acsami.5b08600
41. Li, C., Liu, J., Qu, X., Guo, B., Yang, Z.: Polymer-modified halloysite composite nanotubes. J. Appl. Polym. Sci. **110**(6), 3638–3646 (2008). https://doi.org/10.1002/app.28879
42. Li, C., Liu, J., Qu, X., Yang, Z.: A general synthesis approach toward halloysite-based composite nanotube. J. Appl. Polym. Sci. **112**(5), 2647–2655 (2009). https://doi.org/10.1002/app.29652
43. Zhang, J., Zhang, D., Zhang, A., Jia, Z., Jia, D.: Dendritic polyamidoamine-grafted halloysite nanotubes for fabricating toughened epoxy composites. Iran. Polym. J. **22**(7), 501–510 (2013). https://doi.org/10.1007/s13726-013-0151-5
44. Bertolino, V., Cavallaro, G., Lazzara, G., Merli, M., Milioto, S., Parisi, F., Sciascia, L.: Effect of the biopolymer charge and the nanoclay morphology on nanocomposite materials. Ind. Eng. Chem. Res. **55**(27), 7373–7380 (2016). https://doi.org/10.1021/acs.iecr.6b01816
45. Cavallaro, G., Lazzara, G., Milioto, S., Parisi, F.: Steric stabilization of modified nanoclays triggered by temperature. J. Colloid Interface Sci. **461**, 346–351 (2016). https://doi.org/10.1016/j.jcis.2015.09.046
46. Liu, F., Bai, L., Zhang, H., Song, H., Hu, L., Wu, Y., Ba, X.: Smart H_2O_2-responsive drug delivery system made by halloysite nanotubes and carbohydrate polymers. ACS Appl. Mater. Interfaces **9**(37), 31626–31633 (2017). https://doi.org/10.1021/acsami.7b10867
47. Massaro, M., Riela, S., Lazzara, G., Gruttadauria, M., Milioto, S., Noto, R.: Green conditions for the Suzuki reaction using microwave irradiation and a new HNT-supported ionic liquid-like phase (HNT-SILLP) catalyst. Appl. Organomet. Chem. **28**(4), 234–238 (2014). https://doi.org/10.1002/aoc.3114
48. Massaro, M., Riela, S., Lo Meo, P., Noto, R., Cavallaro, G., Milioto, S., Lazzara, G.: Functionalized halloysite multivalent glycocluster as a new drug delivery system. J. Mater. Chem. B **2**(44), 7732–7738 (2014). https://doi.org/10.1039/C4TB01272K
49. Wu, S., Qiu, M., Guo, B., Zhang, L., Lvov, Y.: Nanodot-loaded clay nanotubes as green and sustained radical scavengers for elastomer. ACS Sustain Chem Eng **5**(2), 1775–1783 (2017). https://doi.org/10.1021/acssuschemeng.6b02523
50. Liu, M., Guo, B., Zou, Q., Du, M., Jia, D.: Interactions between halloysite nanotubes and 2, 5-bis (2-benzoxazolyl) thiophene and their effects on reinforcement of polypropylene/halloysite nanocomposites. Nanotechnology **19**(20), 205709 (2008)

51. Dedzo, G.K., Ngnie, G., Detellier, C.: PdNP decoration of halloysite lumen via selective grafting of ionic liquid onto the aluminol surfaces and catalytic application. ACS Appl. Mater. Interfaces **8**(7), 4862–4869 (2016). https://doi.org/10.1021/acsami.5b10407
52. Cao, X.T., Showkat, A.M., Kim, D.W., Jeong, Y.T., Kim, J.S., Lim, K.T.: Preparation of β-cyclodextrin multi-decorated halloysite nanotubes as a catalyst and nanoadsorbent for dye removal. J. Nanosci. Nanotechnol. **15**(11), 8617–8621 (2015). https://doi.org/10.1166/jnn.2015.11482
53. Biddeci, G., Cavallaro, G., Di Blasi, F., Lazzara, G., Massaro, M., Milioto, S., Parisi, F., Riela, S., Spinelli, G.: Halloysite nanotubes loaded with peppermint essential oil as filler for functional biopolymer film. Carbohydr. Polym. **152**, 548–557 (2016). https://doi.org/10.1016/j.carbpol.2016.07.041
54. Massaro, M., Riela, S., Cavallaro, G., Colletti, C.G., Milioto, S., Noto, R., Lazzara, G.: Ecocompatible halloysite/cucurbit[8]uril hybrid as efficient nanosponge for pollutants removal. ChemistrySelect **1**(8), 1773–1779 (2016). https://doi.org/10.1002/slct.201600322
55. Liu, M., Guo, B., Du, M., Lei, Y., Jia, D.: Natural inorganic nanotubes reinforced epoxy resin nanocomposites. J. Polym. Res. **15**(3), 205–212 (2008). https://doi.org/10.1007/s10965-007-9160-4
56. Hou, Y., Jiang, J., Li, K., Zhang, Y., Liu, J.: Grafting amphiphilic brushes onto halloysite nanotubes via a living RAFT polymerization and their pickering emulsification behavior. J. Phys. Chem. B **118**(7), 1962–1967 (2014). https://doi.org/10.1021/jp411610a
57. Türkmen, D., Bakhshpour, M., Akgönüllü, S., Aşır, S., Denizli, A.: Heavy metal ions removal from wastewater using cryogels: a review. Front. Sustain. **3** (2022). https://doi.org/10.3389/frsus.2022.765592
58. Zhu, K., Duan, Y., Wang, F., Gao, P., Jia, H., Ma, C., Wang, C.: Silane-modified halloysite/Fe_3O_4 nanocomposites: simultaneous removal of Cr(VI) and Sb(V) and positive effects of Cr(VI) on Sb(V) adsorption. Chem. Eng. J. **311**, 236–246 (2017). https://doi.org/10.1016/j.cej.2016.11.101
59. Wang, Y., Zhang, X., Wang, Q., Zhang, B., Liu, J.: Continuous fixed bed adsorption of Cu(II) by halloysite nanotube-alginate hybrid beads: an experimental and modelling study. Water Sci. Technol. **70**(2), 192–199 (2014). https://doi.org/10.2166/wst.2014.148
60. Hebbar, R.S., Isloor, A.M., Ananda, K., Ismail, A.F.: Fabrication of polydopamine functionalized halloysite nanotube/polyetherimide membranes for heavy metal removal. J. Mater. Chem. A **4**(3), 764–774 (2016). https://doi.org/10.1039/C5TA09281G
61. Zeng, G., He, Y., Zhan, Y., Zhang, L., Pan, Y., Zhang, C., Yu, Z.: Novel polyvinylidene fluoride nanofiltration membrane blended with functionalized halloysite nanotubes for dye and heavy metal ions removal. J. Hazard. Mater. **317**, 60–72 (2016). https://doi.org/10.1016/j.jhazmat.2016.05.049
62. Meng, Q., Chen, H., Lin, J., Lin, Z., Sun, J.: Zeolite A synthesized from alkaline assisted pre-activated halloysite for efficient heavy metal removal in polluted river water and industrial wastewater. J. Environ. Sci. https://doi.org/10.1016/j.jes.2016.10.010
63. Maziarz, P., Matusik, J.: The effect of acid activation and calcination of halloysite on the efficiency and selectivity of Pb(II), Cd(II), Zn(II) and As(V) uptake. Clay Miner. **51**(3), 385–394 (2016). https://doi.org/10.1180/claymin.2016.051.3.06
64. Tekay, E., Şen, S., Aydınoğlu, D., Nugay, N.: Biosorbent immobilized nanotube reinforced hydrogel carriers for heavy metal removal processes. e-Polymers **16**(1), 15 (2016)
65. Kurczewska, J., Grzesiak, P., Łukaszyk, J., Gabała, E., Schroeder, G.: High decrease in soil metal bioavailability by metal immobilization with halloysite clay. Environ. Chem. Lett. **13**(3), 319–325 (2015). https://doi.org/10.1007/s10311-015-0504-8
66. Matusik, J., Wścisło, A.: Enhanced heavy metal adsorption on functionalized nanotubular halloysite interlayer grafted with aminoalcohols. Appl. Clay Sci. **100**, 50–59 (2014). https://doi.org/10.1016/j.clay.2014.06.034
67. Jinhua, W., Xiang, Z., Bing, Z., Yafei, Z., Rui, Z., Jindun, L., Rongfeng, C.: Rapid adsorption of Cr (VI) on modified halloysite nanotubes. Desalination **259**(1–3), 22–28 (2010). https://doi.org/10.1016/j.desal.2010.04.046

68. Chiew, C.S.C., Yeoh, H.K., Pasbakhsh, P., Krishnaiah, K., Poh, P.E., Tey, B.T., Chan, E.S.: Halloysite/alginate nanocomposite beads: kinetics, equilibrium and mechanism for lead adsorption. Appl. Clay Sci. **119**, 301–310 (2016). https://doi.org/10.1016/j.clay.2015.10.032
69. Ballav, N., Choi, H.J., Mishra, S.B., Maity, A.: Polypyrrole-coated halloysite nanotube clay nanocomposite: synthesis, characterization and Cr(VI) adsorption behaviour. Appl. Clay Sci. **102**, 60–70 (2014). https://doi.org/10.1016/j.clay.2014.10.008
70. Cataldo, S., Lazzara, G., Massaro, M., Muratore, N., Pettignano, A., Riela, S.: Functionalized halloysite nanotubes for enhanced removal of lead(II) ions from aqueous solutions. Appl. Clay Sci. **156**, 87–95 (2018). https://doi.org/10.1016/j.clay.2018.01.028
71. Luo, P., Zhang, J.-S., Zhang, B., Wang, J.-H., Zhao, Y.-F., Liu, J.-D.: Preparation and characterization of silane coupling agent modified halloysite for Cr(VI) removal. Ind. Eng. Chem. Res. **50**(17), 10246–10252 (2011). https://doi.org/10.1021/ie200951n
72. Massaro, M., Noto, R., Riela, S.: Past, present and future perspectives on halloysite clay minerals. Molecules **25**(20) (2020). https://doi.org/10.3390/molecules25204863
73. Cataldo, S., Crea, F., Massaro, M., Milea, D., Pettignano, A., Riela, S.: Functionalized halloysite nanotubes for enhanced removal of Hg^{2+} ions from aqueous solutions. Clays Clay Miner. **69**(1), 117–127 (2021). https://doi.org/10.1007/s42860-021-00112-1
74. Zhao, S., Yuan, Y., Yu, Q., Niu, B., Liao, J., Guo, Z., Wang, N.: A dual-surface amidoximated halloysite nanotube for high-efficiency economical uranium extraction from seawater. Angew. Chem. Int. Ed. **58**(42), 14979–14985 (2019). https://doi.org/10.1002/anie.201908762
75. Cheng, D., Dai, X., Chen, L., Cui, Y., Qiang, C., Sun, Q., Dai, J.: Thiol-yne click synthesis of polyamide-amine dendritic magnetic halloysite nanotubes for the efficient removal of Pb(II). ACS Sustain. Chem. Eng. **8**(2), 771–781 (2020). https://doi.org/10.1021/acssuschemeng.9b04135
76. Vanden Bilcke, C.: The Stockholm Convention on persistent organic pollutants. Rev. Eur. Community Int. Environ. Law **11**(3), 328–342 (2002). https://doi.org/10.1111/1467-9388.00331
77. El-Shahawi, M.S., Hamza, A., Bashammakh, A.S., Al-Saggaf, W.T.: An overview on the accumulation, distribution, transformations, toxicity and analytical methods for the monitoring of persistent organic pollutants. Talanta **80**(5), 1587–1597 (2010). https://doi.org/10.1016/j.talanta.2009.09.055
78. Betianu, C., Gavrilescu, M.: Persistent organic pollutants in environment: inventory procedures and management in the context of the stockholm convention. Environ. Eng. Manag. J. **5**(5), 1011–1028 (2006). https://doi.org/10.30638/eemj.2006.078
79. Titchou, F.E., Zazou, H., Afanga, H., El Gaayda, J., Akbour, R.A., Hamdani, M.: Removal of Persistent Organic Pollutants (POPs) from water and wastewater by adsorption and electrocoagulation process. Groundw. Sustain. Dev. **13**, 100575 (2021). https://doi.org/10.1016/j.gsd.2021.100575
80. Xie, Y., Qian, D., Wu, D., Ma, X.: Magnetic halloysite nanotubes/iron oxide composites for the adsorption of dyes. Chem. Eng. J. **168**(2), 959–963 (2011). https://doi.org/10.1016/j.cej.2011.02.031
81. Liu, Y., Jiang, X., Li, B., Zhang, X., Liu, T., Yan, X., Ding, J., Cai, Q., Zhang, J.: Halloysite nanotubes@reduced graphene oxide composite for removal of dyes from water and as supercapacitors. J. Mater. Chem. A **2**(12), 4264–4269 (2014). https://doi.org/10.1039/C3TA14594H
82. Pan, J., Yao, H., Xu, L., Ou, H., Huo, P., Li, X., Yan, Y.: Selective recognition of 2,4,6-trichlorophenol by molecularly imprinted polymers based on magnetic halloysite nanotubes composites. J. Phys. Chem. C **115**(13), 5440–5449 (2011). https://doi.org/10.1021/jp111120x
83. Massaro, M., Armetta, F., Cavallaro, G., Chillura Martino, D.F., Gruttadauria, M., Lazzara, G., Riela, S., d'Ischia, M.: Effect of halloysite nanotubes filler on polydopamine properties. J. Colloid Interface Sci. **555**, 394–402 (2019). https://doi.org/10.1016/j.jcis.2019.07.100
84. Massaro, M., Colletti, C.G., Lazzara, G., Guernelli, S., Noto, R., Riela, S.: Synthesis and characterization of halloysite-cyclodextrin nanosponges for enhanced dyes adsorption. ACS Sustain. Chem. Eng. **5**(4), 3346–3352 (2017). https://doi.org/10.1021/acssuschemeng.6b03191

85. Li, X., Yao, C., Lu, X., Hu, Z., Yin, Y., Ni, C.: Halloysite–CeO_2–AgBr nanocomposite for solar light photodegradation of methyl orange. Appl. Clay Sci. **104**, 74–80 (2015). https://doi.org/10.1016/j.clay.2014.11.008
86. Xing, W., Ni, L., Huo, P., Lu, Z., Liu, X., Luo, Y., Yan, Y.: Preparation high photocatalytic activity of CdS/halloysite nanotubes (HNTs) nanocomposites with hydrothermal method. Appl. Surf. Sci. **259**, 698–704 (2012). https://doi.org/10.1016/j.apsusc.2012.07.102
87. Zou, M., Du, M., Zhu, H., Xu, C., Fu, Y.: Green synthesis of halloysite nanotubes supported Ag nanoparticles for photocatalytic decomposition of methylene blue. J. Phys. D: Appl. Phys. **45**(32), 325302 (2012)
88. Li, J., Zhou, M., Ye, Z., Wang, H., Ma, C., Huo, P., Yan, Y.: Enhanced photocatalytic activity of g-C_3N_4-ZnO/HNT composite heterostructure photocatalysts for degradation of tetracycline under visible light irradiation. RSC Adv. **5**(111), 91177–91189 (2015). https://doi.org/10.1039/C5RA17360D
89. Li, C., Zhou, T., Zhu, T., Li, X.: Enhanced visible light photocatalytic activity of polyaniline-crystalline TiO_2-halloysite composite nanotubes by tuning the acid dopant in the preparation. RSC Adv. **5**(119), 98482–98491 (2015). https://doi.org/10.1039/C5RA20024E
90. Jia, L., Zhou, T., Xu, J., Li, X., Dong, K., Huang, J., Xu, Z.: The enhanced catalytic activities of asymmetric Au-Ni nanoparticle decorated halloysite-based nanocomposite for the degradation of organic dyes. Nanoscale Res. Lett. **11**(1), 72 (2016). https://doi.org/10.1186/s11671-016-1252-9
91. Zheng, P., Du, Y., Ma, X.: Selective fabrication of iron oxide particles in halloysite lumen. Mater. Chem. Phys. **151**, 14–17 (2015). https://doi.org/10.1016/j.matchemphys.2014.11.075
92. Xianchu, L.U., Xiuyun, C., Aiping, W., Feiyu, K.: Microstructure and photocatalytic decomposition of methylene blue by TiO_2-mounted halloysite, a natural tubular mineral. Acta Geol. Sin.-Engl. Ed. **80**(2), 278–284 (2006). https://doi.org/10.1111/j.1755-6724.2006.tb00243.x
93. Du, Y., Zheng, P.: Adsorption and photodegradation of methylene blue on TiO_2-halloysite adsorbents. Korean J. Chem. Eng. **31**(11), 2051–2056 (2014). https://doi.org/10.1007/s11814-014-0162-8
94. Jiang, L., Huang, Y., Liu, T.: Enhanced visible-light photocatalytic performance of electrospun carbon-doped TiO_2/halloysite nanotube hybrid nanofibers. J. Colloid Interface Sci. **439**, 62–68 (2015). https://doi.org/10.1016/j.jcis.2014.10.026
95. Zhang, Y., Ouyang, J., Yang, H.: Metal oxide nanoparticles deposited onto carbon-coated halloysite nanotubes. Appl. Clay Sci. **95**, 252–259 (2014). https://doi.org/10.1016/j.clay.2014.04.019
96. Li, X., Zhu, W., Yan, X., Lu, X., Yao, C., Ni, C.: Hierarchical La0.7Ce0.3FeO_3/halloysite nanocomposite for photocatalytic degradation of antibiotics. Appl. Phys. A **122**(8), 723 (2016). https://doi.org/10.1007/s00339-016-0240-3
97. Szczepanik, B., Rogala, P., Słomkiewicz, P.M., Banaś, D., Kubala-Kukuś, A., Stabrawa, I.: Synthesis, characterization and photocatalytic activity of TiO_2-halloysite and Fe_2O_3-halloysite nanocomposites for photodegradation of chloroanilines in water. Appl. Clay Sci. **149**, 118–126 (2017). https://doi.org/10.1016/j.clay.2017.08.016
98. Peng, H., Wu, D., Wan, H., Jia, L., Chen, G., Li, J., Cao, Y., Liu, X., Ma, R.: Facile synthesis and characterization of halloysite@W18O49 nanocomposite with enhanced photocatalytic properties. Appl. Clay Sci. **183**, 105319 (2019). https://doi.org/10.1016/j.clay.2019.105319
99. Zhang, D., Cui, Y., Yang, G., Liu, M., Zhu, G., Sheng, X., Deng, F., Zhou, N., Zhang, X., Wei, Y.: Mussel-inspired fabrication of halloysite nanotube-based magnetic composites as catalysts for highly efficient degradation of organic dyes. Appl. Clay Sci. **198**, 105835 (2020). https://doi.org/10.1016/j.clay.2020.105835
100. Lee, J., Seong, S., Jin, S., Jeong, Y., Noh, J.: Synergetic photocatalytic-activity enhancement of lanthanum doped TiO_2 on halloysite nanocomposites for degradation of organic dye. J. Ind. Eng. Chem. **100**, 126–133 (2021). https://doi.org/10.1016/j.jiec.2021.05.029
101. Das, S., Jana, S.: A tubular nanoreactor directing the formation of in situ iron oxide nanorods with superior photocatalytic activity. Environ. Sci. Nano **4**(3), 596–603 (2017). https://doi.org/10.1039/C6EN00570E

102. Massaro, M., Casiello, M., D'Accolti, L., Lazzara, G., Nacci, A., Nicotra, G., Noto, R., Pettignano, A., Spinella, C., Riela, S.: One-pot synthesis of ZnO nanoparticles supported on halloysite nanotubes for catalytic applications. Appl. Clay Sci. **189** (2020). https://doi.org/10.1016/j.clay.2020.105527
103. Zeng, X., Wang, Q., Wang, H., Yang, Y.: Catalytically active silver nanoparticles loaded in the lumen of halloysite nanotubes via electrostatic interactions. J. Mater. Sci. **52**(14), 8391–8400 (2017). https://doi.org/10.1007/s10853-017-1073-y
104. Zhang, M., Su, X., Ma, L., Khan, A., Wang, L., Wang, J., Maloletnev, A.S., Yang, C.: Promotion effects of halloysite nanotubes on catalytic activity of Co_3O_4 nanoparticles toward reduction of 4-nitrophenol and organic dyes. J. Hazard. Mater. **403**, 123870 (2021). https://doi.org/10.1016/j.jhazmat.2020.123870
105. Massaro, M., Colletti, C.G., Fiore, B., La Parola, V., Lazzara, G., Guernelli, S., Zaccheroni, N., Riela, S.: Gold nanoparticles stabilized by modified halloysite nanotubes for catalytic applications. Appl. Organomet. Chem. **33**(3) (2019). https://doi.org/10.1002/aoc.4665
106. Mellouk, S., Belhakem, A., Marouf-Khelifa, K., Schott, J., Khelifa, A.: Cu(II) adsorption by halloysites intercalated with sodium acetate. J. Colloid Interface Sci. **360**(2), 716–724 (2011). https://doi.org/10.1016/j.jcis.2011.05.001
107. Szczepanik, B., Słomkiewicz, P., Garnuszek, M., Czech, K.: Adsorption of chloroanilines from aqueous solutions on the modified halloysite. Appl. Clay Sci. **101**, 260–264 (2014). https://doi.org/10.1016/j.clay.2014.08.013
108. Bellani, L., Giorgetti, L., Riela, S., Lazzara, G., Scialabba, A., Massaro, M.: Ecotoxicity of halloysite nanotube–supported palladium nanoparticles in Raphanus sativus L. Environ. Toxicol. Chem. **35**(10), 2503–2510 (2016). https://doi.org/10.1002/etc.3412
109. Huang, X., Huang, Y., Wang, D., Liu, M., Li, J., Chen, D.: Cellular response of freshwater algae to halloysite nanotubes: alteration of oxidative stress and membrane function. Environ. Sci. Nano **8**(11), 3262–3272 (2021). https://doi.org/10.1039/D1EN00531F
110. Chen, L., Guo, Z., Lao, B., Li, C., Zhu, J., Yu, R., Liu, M.: Phytotoxicity of halloysite nanotubes using wheat as a model: seed germination and growth. Environ. Sci. Nano **8**(10), 3015–3027 (2021). https://doi.org/10.1039/D1EN00507C
111. Teng, G., Chen, C., Jing, N., Chen, C., Duan, Y., Zhang, L., Wu, Z., Zhang, J.: Halloysite nanotubes-based composite material with acid/alkali dual pH response and foliar adhesion for smart delivery of hydrophobic pesticide. Chem. Eng. J. **451**, 139052 (2023). https://doi.org/10.1016/j.cej.2022.139052
112. Qin, Y., An, T., Cheng, H., Su, W., Meng, G., Wu, J., Guo, X., Liu, Z.: Functionalized halloysite nanotubes as chlorpyrifos carriers with high adhesion and temperature response for controlling of beet armyworm. Appl. Clay Sci. **222**, 106488 (2022). https://doi.org/10.1016/j.clay.2022.106488
113. Chen, L., Huang, J., Chen, J., Shi, Q., Chen, T., Qi, G., Liu, M.: Halloysite nanotube-based pesticide formulations with enhanced rain erosion resistance, foliar adhesion, and insecticidal effect. ACS Appl. Mater. Interfaces **14**(36), 41605–41617 (2022). https://doi.org/10.1021/acsami.2c11234
114. Massaro, M., Pieraccini, S., Guernelli, S., Dindo, M.L., Francati, S., Liotta, L.F., Colletti, G.C., Masiero, S., Riela, S.: Photostability assessment of natural pyrethrins using halloysite nanotube carrier system. Appl. Clay Sci. **230**, 106719 (2022). https://doi.org/10.1016/j.clay.2022.106719
115. Zhang, J., Zhou, C.H., Petit, S., Zhang, H.: Hectorite: synthesis, modification, assembly and applications. Appl. Clay Sci. **177**, 114–138 (2019). https://doi.org/10.1016/j.clay.2019.05.001
116. Colletti, C.G., Massaro, M., Lazzara, G., Cavallaro, G., Milioto, S., Pibiri, I., Noto, R., Riela, S.: Synthesis, characterization and study of covalently modified triazole LAPONITE® edges. Appl. Clay Sci. **187** (2020). https://doi.org/10.1016/j.clay.2020.105489
117. Notarbartolo, M., Massaro, M., de Melo Barbosa, R., Emili, C., Liotta, L.F., Poma, P., Raymo, F.M., Sànchez-Espejo, R., Vago, R., Viseras-Iborra, C., Riela, S.: Exploring the cellular uptake of hectorite clay mineral and its drug carrier capabilities. Colloids Surf. B: Biointerfaces, 112931 (2022). https://doi.org/10.1016/j.colsurfb.2022.112931

118. Delavernhe, L., Pilavtepe, M., Emmerich, K.: Cation exchange capacity of natural and synthetic hectorite. Appl. Clay Sci. **151**, 175–180 (2018). https://doi.org/10.1016/j.clay.2017.10.007
119. Hegyesi, N., Vad, R.T., Pukánszky, B.: Determination of the specific surface area of layered silicates by methylene blue adsorption: the role of structure, pH and layer charge. Appl. Clay Sci. **146**, 50–55 (2017). https://doi.org/10.1016/j.clay.2017.05.007
120. Phothitontimongkol, T., Siebers, N., Sukpirom, N., Unob, F.: Preparation and characterization of novel organo-clay minerals for Hg(II) ions adsorption from aqueous solution. Appl. Clay Sci. **43**(3), 343–349 (2009). https://doi.org/10.1016/j.clay.2008.09.016
121. Yue, D., Jing, Y., Ma, J., Xia, C., Yin, X., Jia, Y.: Removal of Neutral Red from aqueous solution by using modified hectorite. Desalination **267**(1), 9–15 (2011). https://doi.org/10.1016/j.desal.2010.08.038
122. Massaro, M., Viseras Iborra, C., Cavallaro, G., Colletti, C.G., García-Villén, F., Lazzara, G., Riela, S.: Synthesis and characterization of nanomaterial based on halloysite and hectorite clay minerals covalently bridged. Nanomaterials **11**(2), 506 (2021)

Organoclay with Surfactants: Detoxification of Hazardous Compounds

Anusha Ekanayake, Anushka Upamali Rajapaksha, and Meththika Vithanage

Abstract The synthesis of organoclays by intercalation of surfactants and their application for environmental remediation has attracted a great deal of attention recently. Organoclays have demonstrated promising sorption capacities for a variety of organic compounds, particularly hydrophobic chemicals, as well as for inorganic metals and anions. There are still some gaps in our knowledge of the molecular mechanisms underlying the synthesis of organoclays and contaminant removal by these substances. In this context, this chapter gives an overview of the preparation, applications, and limits of organoclay materials in environmental remediation. This work revealed that the sorption efficiency depends on the nature of the organoclay, type of pollutant, pH, contact time, and concentration of pollutant. The adsorption of pollutants on organoclay is governed by a variety of mechanisms, depending on the type of pollutant and the physicochemical characteristics of the organoclay, including hydrophobic interactions, ion exchange, and electrostatic interactions. Despite the wealth of knowledge on the formation, characteristics, and application of organoclays as adsorbents, some problems remain unresolved. The use of organoclays seems to be restricted to batch experiments and has not yet been researched under dynamic conditions that would reduce the efficiency of adsorption which indicates the need for pilot and field scale studies to evaluate the efficacy of modified organoclays in removing contaminants under various environmental conditions in the future.

Keywords Adsorption · Environmental remediation · Organoclays · Surfactants

---

A. Ekanayake · A. U. Rajapaksha · M. Vithanage (✉)
Ecosphere Resilience Research Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, Gangodawila 10250, Nugegoda, Sri Lanka
e-mail: meththika@sjp.ac.lk

A. U. Rajapaksha
Instrument Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, Gangodawila 10250, Nugegoda, Sri Lanka

M. Vithanage
Sustainability Cluster, School of Engineering, University of Petroleum and Energy Studies, Dehradun, Uttarakhand 248007, India

Institute of Agriculture, University of Western Australia, Perth WA6009, Australia

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_10

1 Introduction

Clay minerals are used as effective adsorbents for the elimination of various organic and inorganic micropollutants in different environmental systems concerning their availability, non-toxicity, low cost, and high adsorptive and ion exchange properties [1]. The sorptive capacity of layered clay minerals is related to their large specific surface area, cation exchange capacity (CEC), small particle size, reactive functional groups, swelling and hydration properties, and multiple adsorption sites [2, 3]. Natural clays are known as phyllosilicates composed of hydrated aluminosilicates and weathered rocks. The layered molecular structure of clay minerals is based on the stacking of two basic sheets of SiO_4 tetrahedron and $Al(OH)_3$ octahedrons which are held together by van der Waals forces between oxygen and hydroxyl molecules forming an interlayer of water molecules [4] (Fig. 1). The hydrophilic and polar nature of the outer and inner surfaces of the majority of clay minerals results in strong affinities for low- and high-molecular weight, primarily cationic organic compounds. However, the negative charge of the clay minerals has restricted their application in the remediation of anionic pollutants [5]. The exchangeable cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+} which occupy the interlayer sites of clay minerals balanced the excess negative charge of clays [5]. These charge-balancing cations/counter ions form bonds with water molecules, making the clays hydrophilic [1]. Therefore, the reactivity of clay minerals toward non-ionic organic molecules is reduced, which are essentially hydrophobic in the presence of water and do not effectively compete with water [6].

Recent research has focused on enhancing the mechanical properties of clay through different types of modifications to increase their suitability for removing a variety of contaminants, including anionic and non-ionic pollutants [7]. A variety of mechanical, physical, and chemical methods are used to modify clay materials. Clay is physically modified through techniques including grinding and heat activation, which alter the physiochemical properties of clay minerals such as surface

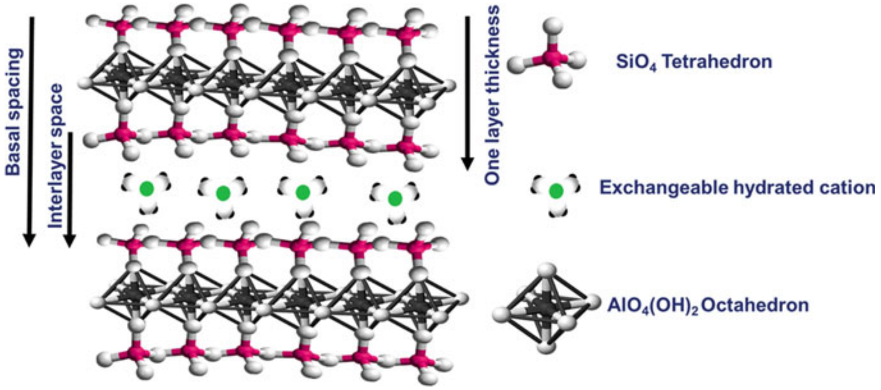


Fig. 1 The structure of 2:1 type clay mineral

area, swelling, porosity, and water dispersibility [8]. Further modification of clay minerals could be achieved via chemical processes such as acid activation, intercalation, and pillaring of organic molecules, or depositing external nanoparticles on surfaces to achieve the desired surface characteristics for the optimal immobilization of particular contaminants [9, 10].

The introduction of long-chain organic compounds has increased the sorption capacities of clay minerals toward hydrophobic organic compounds by refining their pore structure and imparting hydrophobic properties to the clay surface [11, 12]. The resulting modified clays are known as organoclays [4]. Several surfactants have been used to modify clay minerals over the years, including cationic [13], anionic [14], nonionic [15], and zwitterionic [16, 17] surfactants with different lengths and numbers of alkyl chains. It has been shown that the species in the interlayer have a significant impact on the structural features of the resultant organoclays [17].

Montmorillonite (Mnt) has taken the lead among all other expandable clay minerals in the synthesis of organoclays due to its charge density, cation exchange capacity (CEC), propensity for intercalating simple and polymeric organic compounds, swelling ability, availability in the ground, and low cost [18–20].

2 Modification of Surfactant-Based Organoclay

The term ‘organoclays’ denotes a group of modified clays prepared by substituting organic molecules for inorganic cations in a cation exchange reaction [18, 21]. Organoclays synthesized by the association of clay minerals with surfactants are often employed in the development of polymer nanocomposites [22], remediation of different types of pollutants [23], and several other applications such as rheological control agents; cosmetics; refractory varnish; and paints [24]. Organoclays made from ecofriendly organic compounds such as amino acids (e.g., arginine, lysine) [25], polymers [26], silane agents [27], and vitamins (thiamine) [28] have also been used for the application of contaminant removal.

Surfactants are amphiphilic molecules, containing two parts with opposing polarities: a hydrophilic head group that is attracted to polar phases and a hydrophobic tail group with an affinity for nonpolar phases [29]. The intercalation of surfactants in the internal structure of clay minerals switches the surface properties of the raw clay mineral from hydrophilic to hydrophobic, increases the specific surface area to large extent, and increases the basal spacing exposing more adsorption sites promoting the applicability of clay minerals in different areas [4].

2.1 Organoclays Modified by Single and Dual Cationic Surfactants

The type of clay mineral and chemical composition of the surfactant employed for surface modification are the key determinants of the final properties of organoclays. The synthesis of organoclays with cationic surfactants like quaternary ammonium, which may be readily intercalated into the clay interlayer via cation exchange, has gained great interest as a more contemporary way of preparing organoclays [30, 31]. The basal spacing, surface hydrophobicity, and catalytic properties of natural clay are all impacted by their modification with cationic surfactants [32].

Although cation exchange is the main mechanism governing the adsorption of cationic surfactants by natural clay minerals, electrostatic interactions among negatively charged clay surface and organic cations, and van der Waals forces (hydrogen bonds) between the alkyl chain and the clay surface were also identified as driving forces governed the synthesis of organoclays with cationic surfactants [4, 33].

In the organoclays, short alkyl chain surfactants like benzyltrimethylammonium (BTA), are arranged in a single layer with a limited basal spacing, where the CEC of the clay mineral is the unit of measurement. Thus, a permanent interlayer-free space is created, allowing for the accommodation of a wide range of non-ionic organic substances [4]. The sorption capacity of the modified organoclay is influenced by the size of the intercalated alkylammonium ion as it determines how much interlayer space it occupies [6]. The stoichiometric exchange with the inorganic cations causes the loading of surfactants with long alkyl chains (such as hexadecyltrimethylammonium (HDTMA) and benzyldecyltrimethylammonium (BDTA)) which increases linearly as a function of the CEC and attains a threshold level, which is equal to or greater than the CEC value. With an increase in the long-chain surfactant concentration, it can be arranged differently, such as lateral monolayer(s), bilayer(s), and a paraffin structure inside the interlayer space of organoclays [2, 34] (Fig. 2). In addition to the alkyl chain length of the surfactant, the layer charge of the clay mineral further affects the arrangement of intercalated organic cations in the clay mineral interlayer. The transition from monolayer to bilayer occurs even at smaller chain length values (shorter chain length) as the layer charge increases. In highly charged 2:1 layer silicates, the paraffin-type structure is favored, resulting in broad basal spacings (> 2.2 nm) [6].

Organoclays can be synthesized through a solid-state reaction, a semi-solid state or a suspension with the aqueous suspension approach currently being the most prevalent [35, 36]. In the aqueous suspension method, clay mineral is mixed with a suspension of a cationic surfactant mostly in a microwave heating system which has been useful for complete surface coverage of clay mineral with cationic surfactants [35, 37]. The process of preparing organoclays by solid-state reaction involves adding clay minerals and a cationic modifier to the ball mill and milling those together [38, 39]. The addition of raw clay minerals, a cationic modifier, and a small amount of water to the ball mill will produce a semi-solid-state reaction as an alternative

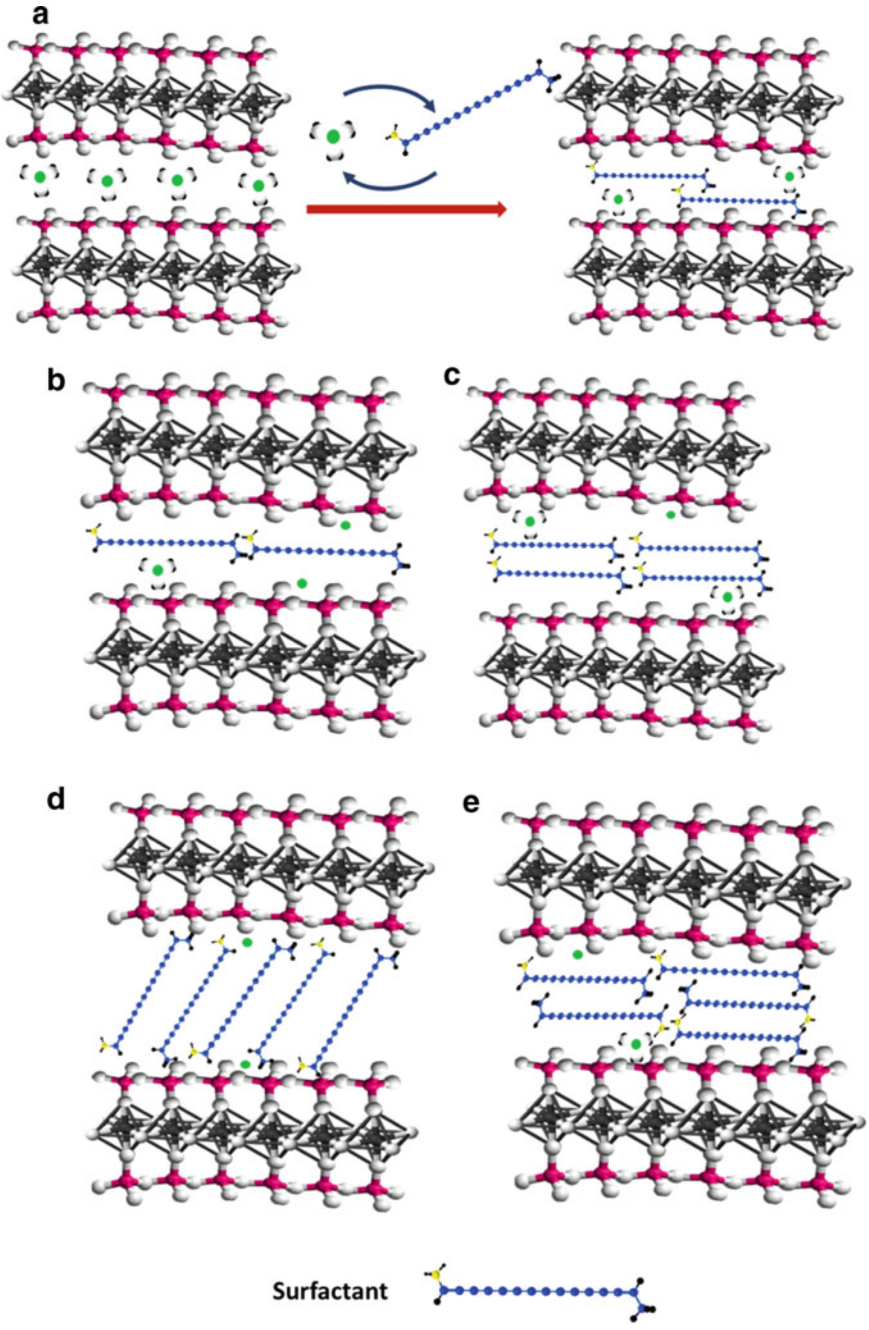


Fig. 2 **a** Schematic representation of formation of organoclay and possible arrangements of long-chain surfactants in the interlayer space of expanding 2:1 layer clay minerals, **b** monolayer, **c** bilayer, **d** paraffin-type, and **e** pseudo-trilayer [1, 6]

technique [39]. Zhou et al. [36] who compared the performances of organoclays prepared from these three different methods reported that organoclays synthesized through the aqueous dispersion method had better properties of a great adsorbent. This was attributed to the even distribution of modifiers in the liquid phase on the surface of organoclay which leads to improved performance.

Surfactant intercalation improves the adsorption performance of organoclays to varying degrees, depending on the chemical composition and structural layout of the intercalated surfactants [2, 40]. For instance, surfactants with long alkyl chains, such as HDTMA, produce a favorable organic environment for the adsorption of alkanes or hydrophobic chemicals in the clay interlayer region, whereas an excellent affinity for aromatic molecules, including phenols, dyes, and other chemicals, is demonstrated by organoclays modified with surfactants containing aromatic rings, such as BDTA or BTA [2, 40, 41].

Thus, cationic organoclays outperform layered double hydroxides in terms of their capacity to adsorb both inorganic (for instance, nitrate and chromates) [42, 43] and organic compounds (diclofenac and phenols) [2, 44]. However, there are limitations with these engineered layered materials (pH condition, affinity to carbonates, etc.), which are primarily intended for laboratory experiments or other technological applications.

2.2 Organoclays Modified by Zwitterionic Surfactants

Due to the non-environmentally friendly nature of cationic surfactants in biomedical applications and the paucity of biocompatibility data in biological sectors, the use of cationic surfactants as modifiers in organoclay synthesis is frequently hampered [45]. Thus the use of alternative surfactants, such as zwitterionic surfactants has become the focus of research on the synthesis of organoclay [4]. The challenge of secondary contamination brought on by the release of surfactants from conventional organoclays can be resolved by the introduction of zwitterionic surfactants, which have excellent water solubility and are biologically safe and biodegradable compounds [46, 47]. Due to their improved biocompatibility and simultaneous presence of both a cationic hydrophobic group and an anionic hydrophilic group, it is expected that organoclays modified by zwitterions will find widespread applications in environmental engineering [45, 48].

The majority of zwitterionic surfactants enter the spacing via exchanging with the inorganic cations in the interlayer space and are adsorbing onto the interlayer cation sites at low surfactant loadings [17]. The second and third driving forces take the stage when the surfactant loading is higher than the CEC of Mnt. The molecules of the surfactant then bind to the surface-adsorbed surfactant via van der Waal forces. While others have adhered to the clay surface, certain surfactants enter the interlayers. However, no apparent exchange of the zwitterionic surfactant with the interlayer Ca^{2+} has occurred during the intercalation of the zwitterionic surfactant 3-(N,N-dimethylpalmityl-ammonio) propane sulfonate (SB 16) to Mnts. Instead of an exchange reaction, an ion–dipole interaction between the head groups of SB16 and the surface of Mnt-containing cations drives the intercalation mechanism for SB16 [49].

Similar to cationic surfactants, zwitterionic surfactants alter the physical properties of clay minerals such as thermal stability [50], hydrophobicity [35], basal spacing, and sorption capacity [32]. Organoclay interlayer phases modified with zwitterionic surfactants had distinct electrochemical characteristics that led to significant sorption capacities for cationic organic contaminants via electrostatic interactions [17]. The zwitterionic surfactant-modified montmorillonites have exhibited a greater interlayer gap at the same surfactant loading level when compared to conventional organo-montmorillonites treated with cationic surfactants [17].

Depending on the level of surfactant loading, the long-chain alkyls of zwitterionic surfactants can adopt various arrangements and configurations. The arrangement of zwitterionic surfactants will shift from monolayer to multilayer models when the loading of surfactants increases from a lower value to a higher CEC [17]. Mnt modified with two zwitterionic surfactants dodecyldimethylbetaine (BS-12) and lauramidopropylbetaine (LAB-35) have shown two different arrangements within the clay interlayer [51]. The configurations of LAB-35 in the organoclay interlayer were inclined and perpendicular to the basal plane of the Mnt, whereas BS-12 was present in both lateral monolayer and flat-lying bilayer forms [51].

The length of the alkyl chain and the amount of the zwitterionic modifier loaded determine how effective the resultant organoclays are at adsorbing pollutants [51, 52]. The resulting organoclay's adsorption efficiency has increased with increasing the loading of zwitterionic surfactant. Anyhow once it reached the maximum it began to decrease with a further increase in surfactant loading [31]. This was attributed to the steric effect that occurs when a large part of the interlayer space of modified clay was occupied by a large number of zwitterions [32]. The adsorption of organic contaminants is promoted by the hydrophobic group of zwitterionic modifiers, whereas the adsorption of heavy metals is facilitated by the hydrophilic group of the same modifiers [32]. Thus, organoclays treated with zwitterionic surfactants show great potential in wastewater treatment for the effective removal of organic pollutants with both negative and positive charges.

2.3 Organoclays Modified by Non-ionic Surfactants

The non-ionic surfactants used in the synthesis of organoclays contain no electric charge across the whole pH range, remaining entirely non-ionic in aqueous systems. Non-ionic surfactants demonstrated interesting characteristics, including high biodegradability, non-toxicity, chemical and thermal stability, and excellent biocompatibility, making them appropriate for application as clay mineral modifiers [40, 53, 54].

It was a subject of debate to understand the driving forces of adsorption of these organo-non-ionic modifiers on hydrophilic clay minerals, either electrostatic interactions or ion–dipole interaction and hydrogen bonds [4]. Calabrese et al. [15], who used non-ionic surfactant Tween 20 to modify natural clay Mnt, found that pH has a significant impact on the amount of surfactant that is adsorbed; the higher the pH, the less surfactant is loaded onto the clay. This finding suggested that the surfactant adsorption on clay is primarily caused by hydrogen bonds between the repeating ether oxygen in the biosurfactant's ethoxylate chains and the aluminols and silanols edge sites on the clay, as well as the water molecules in the hydration sphere of exchangeable cations. Al–OH and Si–OH sites become less accessible with increasing pH, favoring these interactions in an acidic environment. The CEC of Mnt treated with non-ionic surfactants remains unchanged since there is no occurrence of ion exchange when it is intercalated in clay minerals [48, 55, 56].

Greater interlayer spacings were attained in non-ionic surfactant-based organoclays via hydrogen bonding between the oxide and the SiO_2 surface of the clay mineral [57]. The formation of aggregates from the bulk loading of non-ionic surfactants caused broad gaps in the interlayer space that favored the adsorption of contaminants of various kinds, including cationic, hydrophobic, and polar species [4]. Ouellet-Plamondon et al. [57] characterized modified bentonite (Bnt) with three different surfactants, a non-ionic surfactant polypropylene glycol, a cationic surfactant, and an amphiphilic phospholipid surfactant. Upon intercalation of three different surfactants, the basal spacing increased with respect to the concentration, but it was limited to three different intercalation regions; crystalline, osmotic, and extensive regions, respectively. Intercalation of polypropylene glycol at low concentrations (0.05 and 0.10 CEC) increased the basal spacing, and at a concentration of 2.00 CEC, the basal spacing increased from 1.24 nm to 1.83 nm, remaining in the zone of crystalline swelling. Although the polypropylene glycols induced greater intercalation than the cationic and lecithin derivative surfactants at low dosages, they also worked as intercalation inhibitors at higher concentrations, which prevented the basal spacing from expanding over 1.83 nm.

The intercalation of non-ionic surfactant trimethylene glycol mono n-decyl ether, below the critical micelle concentration, has resulted in a lateral monolayer surfactant arrangement within the interlayer space of Mnt suggesting that the arrangement of non-ionic surfactants in the interlayer space is concentration dependent [40]. According to the TGA and FTIR spectra, the PPGs and HDTMA surfactants were arranged orderly in the interlayer space of the Bnt at higher concentrations, whereas the surfactants formed a disordered conformation at lower concentrations that required more energy to break down [57].

Organoclays prepared with non-ionic surfactants lead to a dual hydrophobic/hydrophilic character by preserving the inorganic exchangeable cations. The dual hydrophilic/hydrophobic character of organoclays increased the potential for the adsorption of polar molecules via H-bonding and ion–dipole interactions as well as cationic compounds via cation exchange [4]. A dual-function property was well exhibited by Mnt grafted with a carboxylic group-bearing surfactant, carboxydecyltriethyl-ammonium which shows greater removal capacities for both

Pb^{2+} and non-ionic organic compounds [15]. A study by De Oliveira et al. [58] has demonstrated that non-ionic surfactant organoclays are more effective than natural Mnt clay and cationic surfactant-modified clay at removing cationic, zwitterionic, and neutral compounds in wastewater. A Na Mnt and two of its organoclays prepared with cationic and non-ionic surfactants have been studied for the adsorption of three micropollutants benzene, dimethyl-phthalate, and paraquat. Results of the study indicate that nonionic organoclay was the most polyvalent adsorbent since this hybrid substance was able to adsorb all of the examined organic compounds because of its dual hydrophilic/hydrophobic nature. Non-ionic surfactant modification of the clay minerals is one of the best approaches to improve the clay's ability to sequester a variety of chemicals of different natures while simultaneously improving its ability to disperse in aqueous environments modifying its adsorption capacity [15].

3 Detoxification of Hazardous Compounds

Organoclays are widely used in several applications including pollutant adsorption in environmental systems. A review of the literature reveals that substituting the exchangeable inorganic cations of clay minerals with organic cations can significantly improve the ability to remove various pollutants (including organic contaminants, heavy metals, and inorganic anions) from water (Table 1).

3.1 Organic Pollutants

Remediation of organic pollutants is challenging because of their complicated molecular structure, ability to persist in surface and groundwater without degrading, ability to bio-accumulate in ecosystems, and potential of causing adverse effects on human health and the environment [59, 60]. Organoclays have demonstrated great promise for the removal or immobilization of a wide variety of organic contaminants including phenols, dyes, chlorinated aromatics, pesticides, and pharmaceuticals [6, 61].

Dyes

Dye effluents are widely spread over wastewater due to their extensive application in textile, paints, pharmaceutical, and cosmetic industries, and are also used in food processing, paper, leather, and dye manufacturing industries [62, 63]. Due to their carcinogenic and mutagenic effects on animal health, aquatic species, and the entire ecosystem, these colored chemicals can cause severe problems [64, 65]. When low-cost and ecologically safe sorbents are provided, adsorption is one of the most often utilized methods for lowering dye concentrations to acceptable limits. From this perspective, organoclays have recently been promising materials to utilize as selective dye adsorbents.

Table 1 Applications of organoclays for adsorption of various pollutants

Pollutant	Organoclay type	Initial pollutants concentration (mg L^{-1})	Adsorbent dosage (g L^{-1})	Adsorption capacity (mg g^{-1})/ Removal percentage %	Kinetics	Isotherm	Main mechanism	References
Organic contaminants								
Orange II dye	Bentonites modified with hexadecyltrimethylammonium bromide	100–1000	–	144.08–249.62	–	Langmuir Freundlich	Ion-exchange	[100]
Red 120 dye	Resadiye bentonite treated with NaCl and modified with cetylpyridinium chloride	1.0×10^{-5}–1.4×10^{-4} mol L^{-1}	0.4	81.97	Pseudo-second order	Langmuir	Ion-exchange	[75]
Methyl orange	Montmorillonite modified with cetyl trimethyl ammonium bromide	120	2	128.21	Pseudo-second order	Langmuir	Physical adsorption mechanism	[14]
	Sodium stearate (SSTA)			42.73				
	Mixture of CTMAB and SSTA			149.25				
Methylene blue	Montmorillonite modified with dodecyl sulfobetaine	120	1	254	Pseudo-second order	Langmuir	Ion-exchange	[101]
Herbicide ethofumesate	Bentonite modified with tetramethylammonium	1×10^{-3}–20×10^{-3}	100	0.1 (mcrog/g)	–	Freundlich	–	[102]
	Octyl trimethylammonium			126				
	Octadecyl trimethylammonium			1960				
Herbicide Bentazon	Montmorillonites modified with cetyltrimethylammonium bromide	20	0.5	500	Pseudo-second order	Langmuir	–	[103]
p-nitrophenol	Palygorskite modified with hexadecyltrimethylammonium bromide and sodium dodecyl sulfate	200	1	137.74	Pseudo-second order	Langmuir	–	[104]

(continued)

Table 1 (continued)

Pollutant	Organoclay type	Initial pollutants concentration (mg L^{-1})	Adsorbent dosage (g L^{-1})	Adsorption capacity (mg g^{-1})/ Removal percentage %	Kinetics	Isotherm	Main mechanism	References
Chlorophenols	Na-montmorillonite modified with dodecyltrimethylammonium bromide (DTAB)	50	6.0	331.1–458.2	Pseudo-second order	Langmuir	Partitioning, electrostatic, and van der Waals forces	[88]
	Cetyltrimethylammonium bromide			395–585.8				
Phenol	Montmorillonite modified with hexadecyl tri-methylammonium	10	10	0.118	–	–	–	[105]
4-chlorophenol				0.334				
Toluene	Natural clay modified with didodecyldimethyl ammonium bromide	–	–	2	–	–	Partition	[106]
Amoxicillin	Bentonite modified with HDTMA	50	10	97.9%	First-order and pseudo-second-order	Langmuir	Partition	[107]
Metallic cations and anions								
Chromate	Montmorillonite modified with butane-1,4-bis(dodecyl dimethyl ammonium bromide) (gBDDA) and dodecyl trimethyl ammonium bromide (DTMA)	0–5 mmol/L	5	11.97	Pseudo-second order	Freundlich	Ion-exchange	[108]
Cu(II)	Montmorillonites modified by cationic surfactant (hexadecyltrimethylammonium bromide)	20–140	5	2.94	Pseudo-second order	Langmuir	Ion-exchange	[109]
	zwitterionic surfactant (hexadecyldimethyl (3-sulphonatopropyl) ammonium			14.15				

(continued)

Table 1 (continued)

Pollutant	Organoclay type	Initial pollutants concentration (mg L^{-1})	Adsorbent dosage (g L^{-1})	Adsorption capacity (mg g^{-1})/ Removal percentage %	Kinetics	Isotherm	Main mechanism	References
As(III)	Sericite modified with hexadecyltrimethylammonium bromide	2	2	0.404	Pseudo-second order	Langmuir	Electrostatic attraction	[110]
As(V)				1.161	–	Langmuir	Complexation	
Cu	Bentonite modified with HDTMA	50	10	98.5%	First-order and pseudo-second-order	Freundlich	Ion-exchange	[107]
Sr(II)	Montmorillonite modified with sodium dodecyl sulfate	20–300	2	26.85	Pseudo-second-order	Langmuir	Surface adsorption	[111]
Anions								
Fluoride	Smectitic clay mineral modified with hexadecylpyridinium	1,840	2	27.77	Pseudo-second-order	Langmuir	Ion-exchange	[98]
Phosphate		1,420	2	23.80				
Nitrate	Smectite clay modified with Hexadecylpyridinium (HDPy) bromide	100	2	18.51	Pseudo-second-order	Langmuir and Freundlich	–	[112]
	Hexadecyltrimethylammonium bromide			15.38				

Sorption capacities of clay minerals such as vermiculite (Vmt) [66, 67], Mnt [19, 68], and sepiolite (Sep) [69, 70] modified with cationic, nonionic, and zwitterionic surfactants have been extensively studied toward both anionic [71, 72] and cationic basic dyes [68, 73]. Hisarlı et al. [74] have studied the adsorption of anionic dyes belonging to subclasses of anthraquinone (Lanaset-Green-B), azo (Lanaset-Red-2B), and complex dyes (Lanaset-Red-G) by trimethylammonium (TMA) modified Sep and showed that regardless of the molecular structures of the dyes, tetradecylammonium-modified Sep has the best capacity for all dyes. The mechanism for dye adsorption on surfactant-modified organoclay included ionic interactions between the head groups of the surfactant and dye as well as tail–tail interactions when the surfactant-tail in the first layer was longer than the hydrophobic portion of the dye. The maximum removal capacities for all dyes reported by Sep modified with tetradecyl-TMA were associated with the amount of TMA^+ groups orientated up in the second layer of surfactant, indicating that one TMA^+ group interacts with one sulfonate group independently of the valence of the dye. A study by Tabak et al. [75] investigated the adsorption of the Reactive Red 120 by cetylpyridinium modified Resadiye Bnt (CP-Bnt) and reported a higher uptake of dyes at low pHs. This finding was explained by the mechanism of dye adsorption on organoclay, which is driven by electrostatic interactions between the anionic dye species and the positively charged Bnt surface as well as interactions between the surfactant counterions and the dye. Clay minerals (Vmt, Mnt, and silica nanosheets) modified with a surfactant, 2,2′-bis(dodecyldimethylammonio)-ethyl ether dichloride (BDEE) have been tested for their adsorption capacities toward Congo red. The highest saturated sorption amount was reported by BDEE-Vmt, which was followed by BDEE-Mnt and BDEE-silica nanosheets, decreasing with the precursor layer charge, wettability, and hydrophobicity of particles. Hydrophobic interactions were primarily responsible for Congo red adsorption on organo-clays [76].

Pesticides and Herbicides

Organoclays are effective at eliminating a variety of non-ionic pesticides and herbicides from the environment by preventing their leaching into the water and reducing their volatility through the processes of solute surface interactions and partitioning [77]. The efficacy of organoclay as a sorbent and detoxifying agent of pesticides has been proven by a study by Groisman et al. [78]. Na^+-Mnt intercalated with decyldimethyl-2-aminoethyl ammonium has been utilized for the sorption of pesticides methyl parathion and tetrachlorvinphos. The hydrolysis of sorbed organophosphates on organoclay has catalyzed by the quaternary ammonium ion of the surfactant leading to their detoxification. Sanchez-Martin et al. [79] examined the efficiency of cationic surfactant (octadecyltrimetylammonium bromide) modified clay minerals (Mnt, illite, muscovite, Sep, and palygorskite) for the adsorption of different pesticides (penconazole, linuron, alachlor, atrazine, and metalaxy). The authors of this study have attempted to comprehend how the clay mineral structure (expansible and non-expansible layered, and non-layered), surface area, charge density, and hydrophobicity of the pesticides (Kow) affect the adsorption capacity of organoclays. The findings of the study demonstrate a significant positive relationship between the charge densities of various organoclays and the K_{desom} (Freundlich constant) values. This positive correlation suggests that the charge density of the clay mineral—that is, the level of organic cation saturation in the clay determines the effectiveness of organoclays for the adsorption of pesticides. The clay with the highest surfactant density will have the highest value for K_{desom}, which defines how well the organic phase derived from organic cations partitions the pesticide. The less stability of organophilic pollutants intercalated through hydrophobic interactions (low energy molecular forces) results in the expelling of some of the adsorbed compounds. This property brings the suitability of organoclays as slow-release pesticide carriers, lowering the levels of pesticides in the environment [80].

Pharmaceutical Contaminants

The occurrence and persistence of pharmaceuticals and personal care products (PPCPs) in the aquatic environment have emerged as a major issue due to their potential impact on drinking water supplies, aquatic ecosystems, and human health [81, 82]. As for other organic pollutants, various researchers have reported the successful elimination of PPCPs using organoclay. Lu et al. [83] synthesized organo-Mnts using three different surfactants cetyltrimethyl ammonium bromide (CTMAB), 3-(N,N dimethylhexadecylammonio) propane sulfonate (HDAPS), and 1,3-bis(hexadecyldimethylammonio)-propane dibromide (BHDAP) for the adsorption of sulfamethoxazole (SMX). Results of the study showed that organo-Mnts can be employed as efficient adsorbents to remove SMX. Sorption efficiency was dependent on the surfactant loading amount and pH. The dependency of adsorption capacity on pH was explained by the adsorption mechanism followed by SMX, which is mostly electrostatic attraction with hydrophobic interactions playing a minor role. A commercial organoclay modified with dialkyl dimethylammonium (DMA) was utilized to remove the hormone-disrupting chemical Bisphenol-A (BPA) from the aqueous medium [84]. In this study, spectrogel® type-C organoclay has demonstrated a promising uptake of BPA with a removal percentage of 91.44% at a lower concentration level. The preferential sorption of PPs of various chemical natures by cationic and non-ionic surfactant-modified organoclays was also confirmed by De Oliveira et al. [58]. Thirty different PPs have been removed from wastewater using Na^+ -Mnt and its organoclays synthesized with cationic surfactant BDTA and polyoxyethylene (20)oleyl-ether (Brij-O20) non-ionic surfactants. Since electrostatic interactions were shown to be the primary mechanism governing the adsorption, organic PPs cations were found to be preferentially adsorbed onto Brij-O20-Mnt (due to their dual hydrophilic-hydrophobic nature), whilst anionic PPs displayed a strong attraction toward BDTA-Mt.

Phenols

Due to their acute toxicity and biorecalcitrance, phenolic pollutants are among the most prevalent and dangerous organic pollutants in industrial effluent [85, 86]. Gemini surfactant-based organoclays have been demonstrated to be very efficient in removing aromatic and phenolic impurities [87, 88]. Phenol adsorption capacities for similar organoclay types have been reported to be different depending on the adsorbate hydrophobicity. Hexadecyltrimethylammonium bromide (HDTMAB) modified Bnt has shown great sorption capacities toward phenol and phenolic derivatives, which increased in the order, phenol < p-chlorophenol < 2,4-dichlorophenol in proportion to their hydrophobicities. The removal of the studied phenols by the organo-Bnt was found to be driven by both adsorption and partition of which the adsorption effect was more powerful [89]. Gemini surfactants have shown greater removal efficiencies for phenolic compounds compared with monomeric surfactants [90]. A comparative study performed by Yang et al. [87] on 2,4,6-trichlorophenol adsorption by Mnts modified with surfactants that contain different amounts of head groups and alkyl chains, shows that the number of the alkyl chain of the surfactant and its loaded amount on clay mineral had a considerable impact on the ability of organoclay to adsorb phenols. The hydrophobic partition medium produced by the arrangement of longer alkyl chains inside the clay interlayer, which is prone to adsorbing organic pollutants, was supposed to justify the increased affinity of organoclays treated with surfactants with longer alkyl chains toward organic pollutants. Further, a study by Park et al. [91] suggested that the sorption of p-nitrophenol (PNP) and p-chlorophenol (PCP) on HDTMA intercalated clays is size and shape-dependent, which accounts for the greater affinity HDTMA intercalated clays displayed toward PNP compared to PCP.

3.2 Inorganic Pollutants

Heavy Metals

As notorious pollutants with high toxicity and carcinogenicity, heavy metals including Cr(VI), As(III), Cd(II), Pb(II), Cu(II), Hg(II), and Ni(II) have recently attracted great attention due to their environmental persistence [92, 93]. The removal of heavy metals from water systems through adsorption is one of the best approaches, with functional organoclays as a leading choice.

Heavy metal ions show different affinities to distinct functional groups. Thus, more attention should be given to the structure of the clay minerals and properties of the functional groups of organic modifiers when selecting an adsorbent for the effective removal of heavy metals. Organoclays with anionic surfactants in the interlayer are more effective in the sorption of heavy metals than organoclays intercalated with cationic surfactants since those are not readily exchangeable with heavy metals [6]. Depending on the length of the surfactant's alkyl chain, modification of Vmt clay with Gemini surfactants has significantly increased Pb(II) ion removal. Shorter alkyl chain surfactants have exhibited better adsorption capabilities toward Pb(II), where electrostatic interactions were important to the adsorption process [94]. Metalloids like hexavalent chromium have been effectively immobilized by cationic surfactant-modified organoclays (HDTMA-modified bentonite), which do so by encapsulating the metalloids in the form of HTDMA-chromate salts between the layers of smectite [95]. A study by Tohdee and Kaewsichan [96] compared the Cu(II) and Zn(II) adsorption capacities of natural Bnt and Bnt modified with a cationic surfactant (Bencylhexadecyldimethyl ammonium chloride) and revealed that the modified Bnt had significantly improved adsorption capacities over raw bentonite indicating that organoclays are better adsorbents than natural clays for heavy metal removal.

Anions

Currently, the presence of oxyanions such as fluoride, phosphate, and nitrate in the environment has been identified as one of the acute problems worldwide. Although most anions, such as phosphate, fluoride, and nitrate are essential nutrients in the aquatic environment, their presence in excessive amounts may lead to detrimental effects such as eutrophication causing degradation of water quality [1].

Organoclays intercalated with long-chained surfactants in aqueous systems function as an efficient applicant for the adsorption of anions in aqueous systems [97]. Sorption of anions by cationic organoclays depends on the degree of organic cation loading which is a key prerequisite for the production of positive surface charges or positively charged areas on the clay mineral. To meet the requirement, the degree of occupancy of QACs in organoclay should exceed the CEC of the clay mineral [6]. Yahya et al. [98] prepared an organoclay with smectite using the cationic surfactant hexadecylpyridinium ($HDPy^+$) at different concentrations for phosphate and fluoride removal from wastewater. The results of this study reveal that organo-smectite can act as a successful adsorbent with the optimal conditions of 6 h contact time and acidic pH (pH 3–4). Organo-Mnt modified with cationic Gemini surfactant (butane-1,4-bis(dodecyl dimethyl ammonium bromide) has shown high adsorption capacities for nitrate via adsorption mechanisms such as ion exchange with bromide ion and interactions with $–R_4N^+$ groups in Mnt layers [99].

4 Adsorptive Characteristics of Surfactant-Modified Clays

Depending on their production method (including surfactant loading and the properties of the natural clay used to be modified) or the experimental conditions (solution pH, temperature, initial concentration, adsorbent dosage, and contact time), organoclays had varying sorption capabilities for the removal of same organic contaminants [21, 90]. It is discovered that the adsorption capacity of organoclays for a particular contaminant is significantly influenced by the amount of surfactant loading which is increased with increasing the surfactant loading. This was attributed to either an enhanced partitioning effect at higher surfactant loading or stronger Van der Waals forces between the organoclay surface and the adsorbate [113, 114]. However, it was discovered that once the surfactant loading reached an optimum level, the adsorption capacity began to decrease with subsequent increases in surfactant loading. This is because the mass transfer is limited at larger surfactant loadings [115, 116]. Additionally, the quantity of alkyl groups in the surfactant also affects how quickly the adsorption capacity changes [87].

The structural properties of the natural clay, such as expandability and structural charge, have a significant impact on the capacity of synthesized organoclays for the removal of contaminants. The ratio of Si–O tetrahedra to Al–OH octahedra in the clay mineral structure, as well as the strength of the bond between silicate layers, which is mostly defined by layer charge, have a significant impact on the specific surface areas and cation exchange capacity of the clay mineral [117]. Organoclays prepared with different clay minerals (halloysite, kaolinite, and bentonite) and used for nitrate adsorption have shown different removal capacities for anionic ions from water [118]. This was explained by the fact that bentonite has a greater CEC than kaolinite and halloysite.

The experimental conditions such as pH and temperature of the solution have a significant impact on the adsorption potential of prepared organoclays toward different pollutants [1, 114]. The influence of pH alters both the structure and density of charge of the clay surface, its organoclay derivatives, and the chemical form of the organic adsorbate (anionic, cationic, or neutral) [88]. The removal of the anionic pharmaceutical substance diclofenac using Mnt modified with cationic surfactants BDTA and HDTMA has shown that adsorption efficiency is pH-dependent, with favorable adsorption displayed at a pH over 4.5. (i.e., > pKa of diclofenac). Low pH triggers an attack on the octahedral sheets with the release of cations such as Al^{3+} or Mg^{2+} that can substitute sodium cations, destroying the clay mineral's layered structure. However, in this study, the surfactant intercalation serves as a protective layer over the silicate surface, protecting it from acidic attacks; hence, a change in pH has not resulted in any structural alterations on organoclays. The reduction in the amount of negatively charged diclofenac resulted in a decline in sorption capacity at acidic pH [2]. The adsorption capacity is reported to be less influenced by pH with the increase in surfactant loading concentration [91, 113]. Numerous studies have found that when pH increases, the capacity for the adsorption of phenolic compounds decreases [119]. Phenols are more polar at high pH levels since they are present in ionic forms. Quaternary ammonium cations have a weaker attraction to polar molecules when compared to non-polar molecules, which results in fewer adsorption capacities.

In general, the mobility of organic compounds increases with temperature, making it simpler to adsorb or come into interaction with a surface. Additionally, it lowers the energy of activation of several activities. However, it has been shown that for pollutant adsorption on clay minerals, an increase in temperature reduces the sorption efficiency [120]. Similar research by De Oliveira et al. [2] observed that organoclays (BDTA-Mt and HDTMA-Mt) exhibit a strong affinity to diclofenac at temperatures below 35 °C and that an increase in temperature causes a decrease in the quantity of diclofenac that is adsorbed. The introduction of disorder into the surfactant alkyl chains caused by temperature disrupts the hydrophobic adsorption sites produced by the grafted surfactant cations onto the clay surface, reducing adsorption efficiency at high temperatures.

Additionally, several studies have documented variations in the adsorption capacities of organoclays in response to variations in contact time and adsorbate concentration [84, 114]. Pollutant adsorption by organoclays markedly increased in a short period and finally reached an equilibrium with time. The increase in electrostatic repulsion between the adsorption sites and the adsorbate results in a slow adsorption rate of pollutants as time progresses [87, 121]. The equilibrium uptake of organic contaminants increases with increasing pollutant concentration since the concentration gradient between the bulk solution and the clay surface increases which then declines simultaneously [115].

5 Adsorption Mechanisms

Different mechanisms govern the adsorption of pollutants on organoclay, depending on the type of pollutant and the physicochemical properties of the material (Fig. 3). Organoclays have both cationic and anionic sites. The anionic sites of organoclay are formed by the surfactant's negatively charged head groups, whereas the vacant sites that were not occupied by the surfactant in pristine clay mineral act as cationic sites. Thus, organic compounds that exist in aqueous solutions as neutral, anionic, and cationic molecules may be effectively adsorbed by using organoclays. The removal of organic contaminants can take place either through physical adsorption which was driven by van der Waals forces, or by partitioning of solutes through phases depending on the intercalated surfactant's molecular structure. The mechanism of solute partitioning is dominant when the interlayer gap is occupied with larger organic cations and aggregates to form a hydrophobic/organic phase on the organoclay surface where the soluble organic pollutants partition toward and thus, are immobilized [122]. The mechanism is heavily dependent on the solubility of the organic contaminant [123]. The small organic cations such as benzyltriethylammonium, and TMA remain as isolated entities on exchangeable clay sites, forming porous structures which prefer the adsorption of nonionic solutes via physical sorption [88, 124]. Sarkar et al. [125] studied the effect of the surface charges of organo-Bnt modified with arquad 2HT-75 on the sorption of phenol and PNP. A partition mechanism was predominated when the loading of surfactant exceeds the CEC of clay mineral, while both partition and surface adsorption occurs when surfactants were loaded up to the CEC of the clay. Organo-Bnt modified with HDTMAB acts as a super sorbent for anionic dyes where the removal primarily occurs through anionic exchange between counter-ion bromides in the organo-Bnt with the dye anion [100].

Moreover, recent research has indicated that strong interactions between organic molecules and organoclays may occur through a combination of different mechanisms. CTMA-modified Mnt preferentially adsorbs chlorophenol via a complex mechanism combining the van der Waals forces, electrostatic attraction, and partitioning [88]. The negatively charged adsorbates are more likely to interact electrostatically with the monolayer of CTMA with a positively charged surface that covers the exterior of clay minerals. Furthermore, a work by Zhou et al. [30] demonstrates that two different mechanisms are engaged in the sorption of PNP onto the HDTMA-pillared Mnt. These include the electrostatic interaction of PNP in anionic form and the partition mechanism when it is present as a molecule. Potential mechanisms

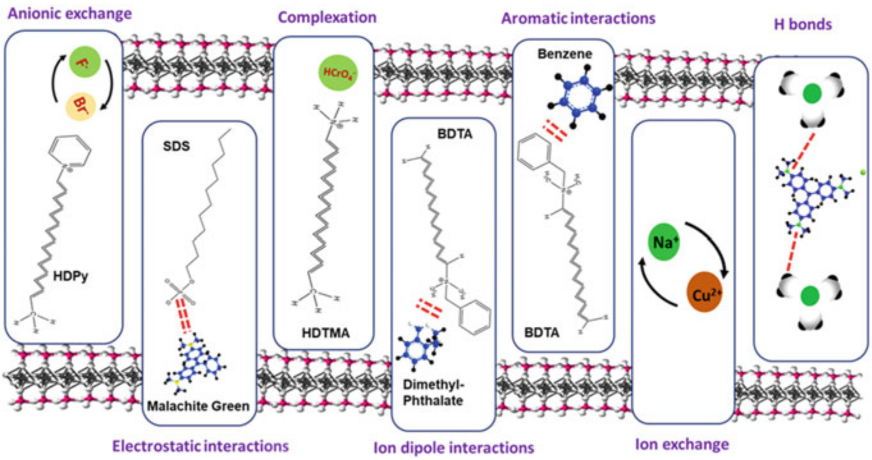


Fig. 3 Adsorption mechanisms followed by organoclays in the removal of pollutants

for the uptake of BPA by the commercial organoclay Spectrogel® type-C modified with DMA were electrostatic forces and hydrophobic interactions. Another potential interaction was the formation of hydrogen bonds between the oxygen of various functional groups of organoclay, such as the Si–O group, and the phenol groups of BPA [84].

Benzyltrimethylammonium bromide (BTMA) modified Bnt has evolved as a new approach to removing dissolved organic carbon from the water. The removal occurs through π–π interactions between aromatic groups and the benzene ring of BTMA [126]. Hexamethylene bispyridinium dibromides modified Mnt have displayed great adsorption capacities for phenol and phenol derivatives such as nitrophenol and chlorophenol [127]. The removal mechanism was supposed to be the π–π polar interactions between the benzene and pyridine rings of the phenols.

Understanding the mechanism of heavy metal retention by functional organoclays is essential for the development of adsorption materials. Surface complexation, precipitation, coordination (chelation), electrostatic adsorption, and ion exchange are the main mechanisms for heavy metal adsorption on organoclays [6]. Using anionic surfactant sodium dodecylsulfate in the treatment of Bnt clay resulted in the effective removal of heavy metals by the formation of surface-cation complexes [128]. Silanol and aluminol groups at the edges of clay minerals which are partially treated with surfactants form inner-sphere complexes with heavy metals since the surfactant molecules only partially occupied the cation exchange sites. The presence of –SH functional groups in modifying organic molecules has facilitated the deliberate sorption of Hg^{2+} by organoclays [124]. Arsenic adsorption on cationic surfactant (octadecyl benzyl dimethyl ammonium) modified organoclay has recently been examined by Su et al. [129]. The effects of ionic strength, pH, and the addition of anions on the effectiveness of As removal by organoclay clearly explain the potential mechanism for the adsorption of As(III) and As(V) on organoclay. The adsorption of

As(V) occurred through the formation of outer-sphere complexes, while adsorption of As(III) occurs via the formation of inter-sphere complexes with Al–O and Si–O groups at the clay edges. Several studies revealed that the retention of heavy metals on functional organoclays often included a combination of numerous mechanisms, with one of them predominates.

The anions such as AsO_3^{-4} and $HCrO_4^-$ can adsorb on the cationic sites of the organoclay by the formation of complexes [21]. Studies by Leyva-Ramos et al. [130] and Majdan et al. [131] have found that sorption of Cr(VI) on HDTMA intercalated organoclays dependent on solution pH, where it adsorbed as chromate or hydrogen chromate depending on the solution pH. The complexation of chromate/hydrogen chromate anions with the quaternary ammonium groups of the organo-Bnt was responsible for the adsorption of Cr(VI) [131]. Hexavalent chromium may be efficiently immobilized by HDTMA-modified Bnt by securing it in the form of salts like HDTMA-chromate between the smectite layers.

6 Limitations

Although organoclays have shown great potential for use in environmental applications, it appears that many challenges limit the use of organoclays in pollutant removal. The sorption characteristics of sorbent systems with organoclays are often studied in solution through batch studies but have not yet been investigated under dynamic conditions that decrease the efficacy of adsorption. Batch experiments conducted at a laboratory scale emphasize the adsorption qualities in a very different way than those undertaken on an industrial scale due to the difficulties in control and variations in the experimental settings in practical application. For example, the efficiency of adsorption under natural environmental settings may be decreased by the adsorption capacities determined from batch experiments carried out without taking experimental parameters like ionic strength into consideration.

Further organoclays have shown some limitations at their high loadings. The majority of the organophilic pollutants are intercalated on organoclays by hydrophobic interactions, which are low-energy molecular forces. As a consequence, some of these contaminants can be easily evacuated from the layered organoclays. A similar reason may cause intercalated cationic surfactants to be expelled from organoclays, which might result in environmental contamination and secondary pollution owing to their chemical nature and toxicity (irritation risk with some cationic surfactants) [4, 18].

The “lock effect,” in which previously intercalated species “lock” the interlayer gap preventing additional species from co-intercalating, may also limit the adsorption capabilities of synthetic organoclays [132]. Different intercalated species compete for the limited interlayer space, and the neighboring intercalated species may produce steric hindrance in the interlayer, inhibiting each other’s activity [90]. Furthermore, electrostatic interactions between adjacent oppositely charged intercalated species have resulted in an unfavorable “neutralization effect”. When intercalating various functional groups in natural clays, these two phenomena have not yet been fully resolved. Yang et al. [16] have concurrently addressed the "lock effect" and "neutralization effect" by synthesizing novel multifunctional adsorbent based on Mnt through intercalation of zwitterionic surfactant (Z16), acid activation by chloric acid, and introduction of hydrated ferric oxides (HFOs).

Despite being enhanced for industrial uses, these modification techniques are either inefficient or unprofitable for low-cost environmental applications. Due to the lack of understanding of how the target pollutant interacts with the organoclay matrix, the use of this technology has not yet reached its full capacity. The reversibility, degradation, transformation, and bioavailability of the sorbed contaminants are also not fully understood. Therefore, it is challenging to determine the best economical modification technique that might enhance the remediation potential of clays. Additional challenges to the widespread commercial usage of organoclays include the difficulties of regeneration and the requirement for the removal of sorbed impurities [124].

7 Concluding Remarks and Future Perspectives

Organoclays have been extensively studied recently for their use in the removal of a variety of pollutants from environmental systems, including organic pollutants, heavy metals, and inorganic anions. These studies provided a clear theoretical foundation for surfactant interactions with clay minerals; however, the practical application of organoclays as adsorbents for pollutant removal is not always straightforward due to the numerous factors involved. The high specificity of organoclays hinders their development and environmental applications for the removal of particular pollutants. Furthermore, there are still gaps in our knowledge of the molecular mechanisms underlying the removal of pollutants by organoclays, particularly with regard to the release and bioavailability of the contaminants that have been sorbed. Even though organoclays are now more widely used as an affordable, non-toxic adsorbent among other adsorbents, more laboratory and extensive research are still needed to replace the currently employed adsorbents like activated carbon. The use of organoclay as an adsorbent to remove dissolved pollutants will result in the leaching of intercalated surfactants causing secondary pollution. This emphasizes the need for further attention regarding the use of environmentally friendly surfactants as intercalating materials in the synthesis of organoclays. It is anticipated that the biodegradable organic compound-containing organoclay will have many uses in environmental engineering. Further, the drawbacks like the difficulty in regenerating and the need to dispose of sorbed contaminants, limit the practical application of organoclays as adsorbents. At the disposal site, the released contaminants may move around presenting a new risk. To resolve the issue, the contaminants that have adhered to the organoclay surface can be converted into non-toxic or less toxic forms. Organoclays can acquire bio-reactivity by being exposed to microorganisms that can successfully convert pollutants into less toxic forms. More research is necessary on these topics in the future because this is currently a cutting-edge interdisciplinary area of study among microbiology and material science. A review of the literature has shown that intercalated surfactant properties, such as alkyl chain length and surfactant concentration, have a significant impact on the prepared organoclays' capacity to adsorb contaminants. Therefore, it is crucial for future research in the design and applications of organoclay to have a thorough understanding of the interdependence of the sorption capacities and intercalated surfactant properties.

References

1. Yahya, K., Hamdi, W., Hamdi, N.: Organoclay nano-adsorbent: preparation. Charact. Appl. (2022). https://doi.org/10.5772/intechopen.105903
2. De Oliveira, T., Guégan, R., Thiebault, T., Le Milbeau, C., Muller, F., Teixeira, V., Giovanela, M., Boussafir, M.: Adsorption of diclofenac onto organoclays: Effects of surfactant and environmental (pH and temperature) conditions. J. Hazard. Mater. **323**, 558–566 (2017). https://doi.org/10.1016/j.jhazmat.2016.05.001
3. Ewis, D., Ba-Abbad, M.M., Benamor, A., El-Naas, M.H.: Adsorption of organic water pollutants by clays and clay minerals composites: a comprehensive review. Appl. Clay Sci. **229**, 106686 (2022). https://doi.org/10.1016/j.clay.2022.106686
4. Guégan, R.: Organoclay applications and limits in the environment. C R Chim. **22**(2–3), 132–141 (2019). https://doi.org/10.1016/j.crci.2018.09.004
5. Kumari, N., Mohan, C.: Basics of clay minerals and their characteristic properties. Clay Clay Miner. **24**, 1–29 (2021)
6. Theng, B.K.G., Churchman, G.J., Gates, W.P., Yuan, G.: Organically modified clays for pollutant uptake and environmental protection. In: Soil Mineral Microbe-Organic Interactions: Theories and Applications, pp. 145–174. Springer (2008). https://doi.org/10.1007/978-3-540-77686-4_6
7. Sarkar, B., Rusmin, R., Ugochukwu, U.C., Mukhopadhyay, R., and Manjaiah, K.M.: Modified clay minerals for environmental applications. In: Modified Clay and Zeolite Nanocomposite Materials, pp. 113–127. Elsevier (2019)
8. Madejová, J., Pálková, H.: NIR contribution to the study of modified clay minerals. Dev. Clay Sci. **8**, 447–481 (2017). https://doi.org/10.1016/B978-0-08-100355-8.00013-8
9. Massaro, M., Cavallaro, G., Colletti, C.G., Lazzara, G., Milioto, S., Noto, R., Riela, S.: Chemical modification of halloysite nanotubes for controlled loading and release. J. Mater. Chem. **6**(21), 3415–3433 (2018). https://doi.org/10.1039/c8tb00543e
10. Moreira, M.A., Ciuffi, K.J., Rives, V., Vicente, M.A., Trujillano, R., Gil, A., Korili, S.A., de Faria, E.H.: Effect of chemical modification of palygorskite and sepiolite by 3-aminopropyltriethoxisilane on adsorption of cationic and anionic dyes. Appl. Clay Sci. **135**, 394–404 (2017). https://doi.org/10.1016/j.clay.2016.10.022
11. Ain, Q.U., Rasheed, U., Yaseen, M., Zhang, H., He, R., Tong, Z.: Fabrication of magnetically separable 3-acrylamidopropyltrimethylammonium chloride intercalated bentonite composite for the efficient adsorption of cationic and anionic dyes. Appl. Surf. Sci. **514**, 145929 (2020). https://doi.org/10.1016/j.apsusc.2020.145929
12. Jankovič, L., Škorňa, P., Rodriguez, D.M., Scholtzová, E., Tunega, D.: Preparation, characterization and adsorption properties of tetraalkylphosphonium organobeidellites. Appl. Clay Sci. **204**, 105989 (2021). https://doi.org/10.1016/j.clay.2021.105989
13. Zhou, L., He, Y., Gou, S., Zhang, Q., Liu, L., Tang, L., Zhou, X., Duan, M.: Efficient inhibition of montmorillonite swelling through controlling flexibly structure of piperazine-based polyether Gemini quaternary ammonium salts. J. Chem. Eng. **383**, 123190 (2020). https://doi.org/10.1016/j.cej.2019.123190

14. Chen, D., Chen, J., Luan, X., Ji, H., Xia, Z.: Characterization of anion–cationic surfactants modified montmorillonite and its application for the removal of methyl orange. J. Chem. Eng. **171**(3), 1150–1158 (2011). https://doi.org/10.1016/j.cej.2011.05.013
15. Calabrese, I., Cavallaro, G., Lazzara, G., Merli, M., Sciascia, L., Turco Liveri, M.L.: Preparation and characterization of bio-organoclays using nonionic surfactant. Adsorption 22(2), 105–116 (2016). https://doi.org/10.1007/s10450-015-9697-1
16. Yang, Y., Zhu, R., Chen, Q., Xing, J., Ma, L., He, Q., Fan, J., Xi, Y., Zhu, J., He, H.: Development of novel multifunctional adsorbent by effectively hosting both zwitterionic surfactant and hydrated ferric oxides in montmorillonite. Sci. Total Environ. **774**, 144974 (2021). https://doi.org/10.1016/j.scitotenv.2021.144974
17. Zhu, J., Qing, Y., Wang, T., Zhu, R., Wei, J., Tao, Q., Yuan, P., He, H.: Preparation and characterization of zwitterionic surfactant-modified montmorillonites. J. Colloid Interf. Sci. **360**(2), 386–392 (2011). https://doi.org/10.1016/j.jcis.2011.04.069
18. He, H., Ma, L., Zhu, J., Frost, R.L., Theng, B.K.G., Bergaya, F.: Synthesis of organoclays: a critical review and some unresolved issues. Appl. Clay Sci. **100**, 22–28 (2014). https://doi.org/10.1016/j.clay.2014.02.008
19. Huang, P., Kazlauciunas, A., Menzel, R., Lin, L.: Determining the mechanism and efficiency of industrial dye adsorption through facile structural control of organo-montmorillonite adsorbents. ACS Appl. Mater. Interf. **9**(31), 26383–26391 (2017). https://doi.org/10.1021/acsami.7b08406
20. Ugochukwu, U.C., Fialips, C.I.: Removal of crude oil polycyclic aromatic hydrocarbons via organoclay-microbe-oil interactions. Chemosphere **174**, 28–38 (2017). https://doi.org/10.1016/j.chemosphere.2017.01.080
21. Leyva-Ramos, R., Jacobo-Azuara, A., Martínez-Costa, J.I.: Organoclays. Fundamentals and applications for removing toxic pollutants from water solution. In: Porous Materials, pp. 341–363. Springer (2021). https://doi.org/10.1007/978-3-030-65991-2_13
22. Rigail-Cedeño, A., Vera-Sorroche, J., García-Mejía, G., Intriago, R.: Effect of the intercalation and dispersion of organoclays on energy demand in the extrusion of recycled HDPE/PP nanocomposites. Energies **15**(3), 859 (2022). https://doi.org/10.3390/en15030859
23. Otunola, B.O., Ololade, O.O.: A review on the application of clay minerals as heavy metal adsorbents for remediation purposes. Environ. Technol. Innov. **18**, 100692 (2020). https://doi.org/10.1016/j.eti.2020.100692
24. de Paiva, L.B., Morales, A.R., Valenzuela Díaz, F.R.: Organoclays: properties, preparation and applications. Appl. Clay Sci. **42**(1), 8–24 (2008). https://doi.org/10.1016/j.clay.2008.02.006
25. Shokri, E., Yegani, R., Pourabbas, B., Ghofrani, B.: Evaluation of modified montmorillonite with di-cationic surfactants as efficient and environmentally friendly adsorbents for arsenic removal from contaminated water. Water Sci. Technol.: Water Supply **18**(2), 460–472 (2018). https://doi.org/10.2166/ws.2017.077
26. Chen, Q., Zhu, R., Zhu, Y., Liu, J., Zhu, L., Ma, L., Chen, M.: Adsorption of polyhydroxy fullerene on polyethylenimine-modified montmorillonite. Appl. Clay Sci. **132**, 412–418 (2016). https://doi.org/10.1016/j.clay.2016.07.007
27. do Nascimento, F.H., de Souza Costa, D.M., Masini, J.C.: Evaluation of thiol-modified vermiculite for removal of Hg(II) from aqueous solutions. Appl. Clay Sci. 124–125, 227–235 (2016). https://doi.org/10.1016/j.clay.2016.02.017
28. Ben Moshe, S., Rytwo, G.: Thiamine-based organoclay for phenol removal from water. Appl. Clay Sci. **155**, 50-56 (2018). https://doi.org/10.1016/j.clay.2018.01.003
29. Shaban, S.M., Kang, J., Kim, D.-H.: Surfactants: recent advances and their applications. Compos. Commun. **22**, 100537 (2020). https://doi.org/10.1016/j.coco.2020.100537
30. Zhou, Q., He, H.P., Zhu, J.X., Shen, W., Frost, R.L., Yuan, P.: Mechanism of p-nitrophenol adsorption from aqueous solution by HDTMA+-pillared montmorillonite—implications for water purification. J. Hazard. Mater. **154**(1–3), 1025–1032 (2008). https://doi.org/10.1016/j.jhazmat.2007.11.009
31. Zhu, J., Qing, Y., Ma, L., Zhu, R., He, H.: The structure of montmorillonites modified with zwitterionic surfactants and their sorption ability. Mineral Petrol. **109**(3), 349–355 (2015). https://doi.org/10.1007/s00710-014-0339-1

32. Guo, Y.X., Liu, J.H., Gates, W.P., Zhou, C.H.: Organo-modification of montmorillonite. Clays Clay Miner. **68**(6), 601–622 (2020). https://doi.org/10.1007/s42860-020-00098-2
33. Lagaly, G., Ogawa, M., Dékány, I.: Clay mineral–organic interactions. In: Developments in Clay Science, pp. 435–505. Elsevier (2013). https://doi.org/10.1016/B978-0-08-098258-8.00015-8
34. De Oliveira, T., Guégan, R.: Coupled organoclay/micelle action for the adsorption of diclofenac. Environ. Sci. Technol. **50**(18), 10209–10215 (2016). https://doi.org/10.1021/acs.est.6b03393
35. Lazorenko, G., Kasprzhitskii, A., Yavna, V.: Synthesis and structural characterization of betaine-and imidazoline-based organoclays. Chem. Phys. Lett. **692**, 264–270 (2018). https://doi.org/10.1016/j.cplett.2017.12.054
36. Zhou, D., Zhang, Z., Tang, J., Wu, S., Zhao, J.: A comparative study performance of cationic organic montmorillonite prepared by different methods. Sci. Eng. Compos **25**(1), 53–58 (2018). https://doi.org/10.1515/secm-2015-0027
37. Zhang, J., Mei, Q., Chen, L., Chen, X., Zu, L.: Thermal analysis of montmorillonite modified by imidazolium. Emerg. Mater. Res. **5**(2), 214–220 (2016). https://doi.org/10.1680/jemmr.15.00083
38. Wei, G., Li, Y., Zhang, L., Cai, S., Zhu, T., Li, Z., Mo, J.: Synthesis of bentonite-supported Fe (II) and heteropolyacid (HPW) composite through a mechanochemical processing. Appl. Clay Sci. **152**, 342–351 (2018). https://doi.org/10.1016/j.clay.2017.11.035
39. Yan, H., Chen, X., Feng, Y., Xiang, F., Li, J., Shi, Z., Wang, X., Lin, Q.: Modification of montmorillonite by ball-milling method for immobilization and delivery of acetamiprid based on alginate/exfoliated montmorillonite nanocomposite. Polym. Bull. **73**(4), 1185–1206 (2016). https://doi.org/10.1007/s00289-015-1542-x
40. Guégan, R., Giovanela, M., Warmont, F., Motelica-Heino, M.: Nonionic organoclay: a 'Swiss Army knife' for the adsorption of organic micro-pollutants? J. Colloid Interf. Sci. **437**, 71–79 (2015). https://doi.org/10.1016/j.jcis.2014.09.043
41. Park, Y., Ayoko, G.A., Frost, R.L.: Application of organoclays for the adsorption of recalcitrant organic molecules from aqueous media. J. Colloid Interf. Sci. **354**(1), 292–305 (2011). https://doi.org/10.1016/j.jcis.2010.09.068
42. Bagherifam, S., Komarneni, S., Lakzian, A., Fotovat, A., Khorasani, R., Huang, W., Ma, J., Hong, S., Cannon, F.S., Wang, Y.: Highly selective removal of nitrate and perchlorate by organoclay. Appl. Clay Sci. **95**, 126–132 (2014). https://doi.org/10.1016/j.clay.2014.03.021
43. Lee, Y.-C., Park, W.-K., Yang, J.-W.: Removal of anionic metals by amino-organoclay for water treatment. J. Hazard. Mater. **190**(1), 652–658 (2011). https://doi.org/10.1016/j.jhazmat.2011.03.093
44. Shah, K.J., Pan, S.-Y., Shukla, A.D., Shah, D.O., Chiang, P.-C.: Mechanism of organic pollutants sorption from aqueous solution by cationic tunable organoclays. J. Colloid Interf. Sci. **529**, 90–99 (2018). https://doi.org/10.1016/j.jcis.2018.05.094
45. Wicklein, B., Darder, M., Aranda, P., Ruiz-Hitzky, E.: Bio-organoclays based on phospholipids as immobilization hosts for biological species. Langmuir **26**(7), 5217–5225 (2010). https://doi.org/10.1021/la9036925
46. Jin, X., Ding, F., Zhao, Q., Shen, T., Mao, S., Gao, M.: Organo-vermiculites modified by zwitterionic gemini surfactants as efficient adsorbents for Congo red. J. Environ. Chem. Eng. **10**(5), 108442 (2022). https://doi.org/10.1016/j.jece.2022.108442
47. Qi, L., Fang, Y., Wang, Z., Ma, N., Jiang, L., Wang, Y.: Synthesis and physicochemical investigation of long alkylchain betaine zwitterionic surfactant. J. Surfactants Deterg. **11**(1), 55–59 (2008). https://doi.org/10.1007/s11743-007-1054-2
48. Wang, G., Lian, C., Xi, Y., Sun, Z., Zheng, S.: Evaluation of nonionic surfactant modified montmorillonite as mycotoxins adsorbent for aflatoxin B1 and zearalenone. J. Colloid Interf. Sci. **518**, 48–56 (2018). https://doi.org/10.1016/j.jcis.2018.02.020
49. Zhu, J., Zhang, P., Qing, Y., Wen, K., Su, X., Ma, L., Wei, J., Liu, H., He, H., Xi, Y.: Novel intercalation mechanism of zwitterionic surfactant modified montmorillonites. Appl. Clay Sci. **141**, 265–271 (2017). https://doi.org/10.1016/j.clay.2017.03.002

50. Ma, L., Zhu, J., He, H., Xi, Y., Zhu, R., Tao, Q., Liu, D.: Thermal analysis evidence for the location of zwitterionic surfactant on clay minerals. Appl. Clay Sci. **112**, 62–67 (2015). https://doi.org/10.1016/j.clay.2015.04.021
51. Wang, G., Xi, Y., Lian, C., Sun, Z., Zheng, S.: Simultaneous detoxification of polar aflatoxin B1 and weak polar zearalenone from simulated gastrointestinal tract by zwitterionic montmorillonites. J. Hazard. Mater. **364**, 227–237 (2019). https://doi.org/10.1016/j.jhazmat.2018.09.071
52. Gu, Z., Gao, M., Lu, L., Liu, Y., Yang, S.: Montmorillonite functionalized with zwitterionic surfactant as a highly efficient adsorbent for herbicides. Ind. Eng. Chem. Res. **54**(18), 4947–4955 (2015). https://doi.org/10.1021/acs.iecr.5b00438
53. Deng, Y., Dixon, J.B., White, G.N.: Bonding mechanisms and conformation of poly (ethylene oxide)-based surfactants in interlayer of smectite. Colloid Polym. Sci. **284**(4), 347–356 (2006). https://doi.org/10.1007/s00396-005-1388-0
54. Guégan, R.: Self-assembly of a non-ionic surfactant onto a clay mineral for the preparation of hybrid layered materials. Soft Matter **9**(45), 10913–10920 (2013). https://doi.org/10.1039/C3SM52337C
55. Guégan, R., De Oliveira, T., Le Gleuher, J., Sugahara, Y.: Tuning down the environmental interests of organoclays for emerging pollutants: pharmaceuticals in presence of electrolytes. Chemosphere **239**, 124730 (2020). https://doi.org/10.1016/j.chemosphere.2019.124730
56. Hojiyev, R., Ulcay, Y., Çelik, M.S.: Development of a clay-polymer compatibility approach for nanocomposite applications. Appl. Clay Sci. **146**, 548–556 (2017). https://doi.org/10.1016/j.clay.2017.07.007
57. Ouellet-Plamondon, C.M., Stasiak, J., and Al-Tabbaa, A.: The effect of cationic, non-ionic and amphiphilic surfactants on the intercalation of bentonite. Colloids Surf, A Physicochem Eng. Asp. **444**, 330–337 (2014). https://doi.org/10.1016/j.colsurfa.2013.12.032
58. De Oliveira, T., Boussafir, M., Fougère, L., Destandau, E., Sugahara, Y., Guégan, R.: Use of a clay mineral and its nonionic and cationic organoclay derivatives for the removal of pharmaceuticals from rural wastewater effluents. Chemosphere **259**, 127480 (2020). https://doi.org/10.1016/j.chemosphere.2020.127480
59. Alharbi, O.M.L., Khattab, R.A., Ali, I.: Health and environmental effects of persistent organic pollutants. J. Mol. Liq. **263**, 442–453 (2018). https://doi.org/10.1016/j.molliq.2018.05.029
60. Gaur, N., Narasimhulu, K., PydiSetty, Y.: Recent advances in the bio-remediation of persistent organic pollutants and its effect on environment. J. Clean. Prod. **198**, 1602–1631 (2018). https://doi.org/10.1016/j.jclepro.2018.07.076
61. Bergaya, F., Lagaly, G.: General introduction: clays, clay minerals, and clay science. In: Developments in Clay Science, pp. 1–19. Elsevier (2013). https://doi.org/10.1016/B978-0-08-098258-8.00001-8
62. Alsantali, R.I., Raja, Q.A., Alzahrani, A.Y.A., Sadiq, A., Naeem, N., Mughal, E.U., Al-Rooqi, M.M., El Guesmi, N., Moussa, Z., Ahmed, S.A.: Miscellaneous azo dyes: a comprehensive review on recent advancements in biological and industrial applications. Dyes Pigm. **199**, 110050 (2022). https://doi.org/10.1016/j.dyepig.2021.110050
63. Benkhaya, S., M'Rabet, S., El Harfi, A.: Classifications, properties, recent synthesis and applications of azo dyes. Heliyon **6**(1), e03271 (2020). https://doi.org/10.1016/j.heliyon.2020.e03271
64. Manzoor, J., Sharma, M.: Impact of textile dyes on human health and environment. In: Impact of Textile Dyes on Public Health and the Environment, pp 162–169. IGI Global (2020). https://doi.org/10.4018/978-1-7998-0311-9.ch008
65. Wani, K.A., Jangid, N.K., Bhat, A.R.: Impact of Textile Dyes on Public Health and the Environment. IGI Global (2019)
66. Shen, T., Wang, L., Zhao, Q., Guo, S., Gao, M.: Single and simultaneous adsorption of basic dyes by novel organo-vermiculite: a combined experimental and theoretical study. Colloids Surf, A Physicochem. Eng. Asp. 601, 125059 (2020). https://doi.org/10.1016/j.colsurfa.2020.125059

67. Stawiński, W., Węgrzyn, A., Dańko, T., Freitas, O., Figueiredo, S., Chmielarz, L.: Acid-base treated vermiculite as high performance adsorbent: insights into the mechanism of cationic dyes adsorption, regeneration, recyclability and stability studies. Chemosphere **173**, 107–115 (2017). https://doi.org/10.1016/j.chemosphere.2017.01.039
68. Haounati, R., Ouachtak, H., El Haouti, R., Akhouairi, S., Largo, F., Akbal, F., Benlhachemi, A., Jada, A., Addi, A.A.: Elaboration and properties of a new SDS/CTAB@ Montmorillonite organoclay composite as a superb adsorbent for the removal of malachite green from aqueous solutions. Sep. Purif. Technol. **255**, 117335 (2021). https://doi.org/10.1016/j.seppur.2020.117335
69. Bhatt, A.S., Sakaria, P.L., Vasudevan, M., Pawar, R.R., Sudheesh, N., Bajaj, H.C., Mody, H.M.: Adsorption of an anionic dye from aqueous medium by organoclays: equilibrium modeling, kinetic and thermodynamic exploration. RSC Adv. **2**(23), 8663–8671 (2012). https://doi.org/10.1039/C2RA20347B
70. Özcan, A., Özcan, A.S.: Adsorption of acid Red 57 from aqueous solutions onto surfactant-modified sepiolite. J. Hazard. Mater. **125**(1–3), 252–259 (2005). https://doi.org/10.1016/j.jhazmat.2005.05.039
71. Choi, N., Son, Y., Kim, T.-H., Park, Y., Hwang, Y.: Adsorption behaviors of modified clays prepared with structurally different surfactants for anionic dyes removal. Environ. Eng. Res. **28**(2), 220076 (2022). https://doi.org/10.4491/eer.2022.076
72. Kooli, F., Liu, Y., Abboudi, M., Rakass, S., Oudghiri Hassani, H., Ibrahim, S.M., Al-Faze, R.: Removal properties of anionic dye eosin by cetyltrimethylammonium organo-clays: the effect of counter-ions and regeneration studies. Molecules **23**(9), 2364 (2018). https://doi.org/10.3390/molecules23092364
73. Tariq, S., Saeed, M., Zahid, U., Munir, M., Intisar, A., Asad Riaz, M., Riaz, A., Waqas, M., Abid, H.M.W.: Green and eco-friendly adsorption of dyes with organoclay: isothermal, kinetic and thermodynamic studies. Toxin Rev. 1–10 (2021). https://doi.org/10.1080/15569543.2021.1975751
74. Hisarlı, G., Atun, G., Ortaboy, S., Tüzün, E.: A systematic study for the removal of anionic dyes by sepiolites modified with a homologous series of trimethylammonium-surfactants from single and binary component solutions. Sep. Sci. Technol. **57**(8), 1304–1326 (2022). https://doi.org/10.1080/01496395.2021.1977825
75. Tabak, A., Baltas, N., Afsin, B., Emirik, M., Caglar, B., Eren, E.: Adsorption of reactive Red 120 from aqueous solutions by cetylpyridinium-bentonite. J. Chem. Technol. Biotechnol. **85**(9), 1199–1207 (2010). https://doi.org/10.1002/jctb.2416
76. Ding, F., Gao, M., Shen, T., Zeng, H., Xiang, Y.: Comparative study of organo-vermiculite, organo-montmorillonite and organo-silica nanosheets functionalized by an ether-spacer-containing Gemini surfactant: Congo red adsorption and wettability. J. Chem. Eng. **349**, 388–396 (2018). https://doi.org/10.1016/j.cej.2018.05.095
77. Carrizosa, M.J., del Carmen Hermosin, M., Koskinen, W.C., Cornejo, J.: Interactions of two sulfonylurea herbicides with organoclays. Clays Clay Miner. **52**(5), 643–649 (2004). https://doi.org/10.1346/CCMN.2004.0520510
78. Groisman, L., Rav-Acha, C., Gerstl, Z., Mingelgrin, U.: Sorption and detoxification of toxic compounds by a bifunctional organoclay. J. Environ. Qual. **33**(5), 1930–1936 (2004). https://doi.org/10.2134/jeq2004.1930
79. Sanchez-Martin, M.J., Rodriguez-Cruz, M.S., Andrades, M.S., Sanchez-Camazano, M.: Efficiency of different clay minerals modified with a cationic surfactant in the adsorption of pesticides: influence of clay type and pesticide hydrophobicity. Appl. Clay Sci. **31**(3–4), 216–228 (2006). https://doi.org/10.1016/j.clay.2005.07.008
80. Nir, S., El Nahhal, Y., Undabeytia, T., Rytwo, G., Polubesova, T., Mishael, Y., Rabinovitz, U., Rubin, B.: Clays and pesticides. Dev. Clay Sci. **1**, 677–691 (2006). https://doi.org/10.1016/S1572-4352(05)01021-4
81. Adeleye, A.S., Xue, J., Zhao, Y., Taylor, A.A., Zenobio, J.E., Sun, Y., Han, Z., Salawu, O.A., Zhu, Y.: Abundance, fate, and effects of pharmaceuticals and personal care products in aquatic environments. J. Hazard. Mater. **424**(Pt B), 127284 (2022). https://doi.org/10.1016/j.jhazmat.2021.127284

82. Cizmas, L., Sharma, V.K., Gray, C.M., McDonald, T.J.: Pharmaceuticals and personal care products in waters: occurrence, toxicity, and risk. Environ. Chem. Lett. **13**(4), 381–394 (2015). https://doi.org/10.1007/s10311-015-0524-4
83. Lu, L., Gao, M., Gu, Z., Yang, S., Liu, Y.: A comparative study and evaluation of sulfamethoxazole adsorption onto organo-montmorillonites. J. Environ. Sci. **26**(12), 2535–2545 (2014). https://doi.org/10.1016/j.jes.2014.04.007
84. De Farias, M.B., Silva, M.G.C., Vieira, M.G.A.: Adsorption of bisphenol A from aqueous solution onto organoclay: experimental design, kinetic, equilibrium and thermodynamic study. Powder Technol. **395**, 695–707 (2022). https://doi.org/10.1016/j.powtec.2021.10.021
85. Zhong, W., Wang, D., Wang, Z.: Distribution and potential ecological risk of 50 phenolic compounds in three rivers in Tianjin China. Environ. Pollut. **235**, 121–128 (2018). https://doi.org/10.1016/j.envpol.2017.12.037
86. Zhou, M., Zhang, J., Sun, C.: Occurrence, ecological and human health risks, and seasonal variations of phenolic compounds in surface water and sediment of a potential polluted river basin in China. IJERPH **14**(10), 1140 (2017). https://doi.org/10.3390/ijerph14101140
87. Yang, Q., Gao, M., Zang, W.: Comparative study of 2, 4, 6-trichlorophenol adsorption by montmorillonites functionalized with surfactants differing in the number of head group and alkyl chain. Colloids Surf, A Physicochem Eng. Asp. **520**, 805–816 (2017). https://doi.org/10.1016/j.colsurfa.2017.02.057
88. Zhang, L., Zhang, B., Wu, T., Sun, D., Li, Y.: Adsorption behavior and mechanism of chlorophenols onto organoclays in aqueous solution. Colloids Surf, A Physicochem. Eng. Asp. **484**, 118–129 (2015). https://doi.org/10.1016/j.colsurfa.2015.07.055
89. Rawajfih, Z., Nsour, N.: Characteristics of phenol and chlorinated phenols sorption onto surfactant-modified bentonite. J. Colloid Interf. Sci. **298**(1), 39–49 (2006). https://doi.org/10.1016/j.jcis.2005.11.063
90. Shen, T., Gao, M.: Gemini surfactant modified organo-clays for removal of organic pollutants from water: a review. J. Chem. Eng. **375**, 121910 (2019). https://doi.org/10.1016/j.cej.2019.121910
91. Park, Y., Ayoko, G.A., Horváth, E., Kurdi, R., Kristof, J., Frost, R.L.: Structural characterisation and environmental application of organoclays for the removal of phenolic compounds. J. Colloid Interf. Sci. **393**, 319–334 (2013). https://doi.org/10.1016/j.jcis.2012.10.067
92. Kumar, V., Pandita, S., Setia, R.: A meta-analysis of potential ecological risk evaluation of heavy metals in sediments and soils. GR (2021). https://doi.org/10.1016/j.gr.2021.10.028
93. Masindi, V., Muedi, K.L.: Environmental contamination by heavy metals. Heavy metals **10**, 115–132 (2018)
94. Han, L., Wang, T., Gong, J., Li, X., Ji, Y., Wang, S.: Multi-hydroxyl containing organo-vermiculites for enhanced adsorption of coexisting methyl blue and Pb (II) and their adsorption mechanisms. Colloids Surf, A Physicochem Eng. Asp. **650**, 129542 (2022). https://doi.org/10.1016/j.colsurfa.2022.129542
95. Krishna, B.S., Murty, D.S.R., Prakash, B.S.J.: Surfactant-modified clay as adsorbent for chromate. Appl. Clay Sci. **20**(1–2), 65–71 (2001). https://doi.org/10.1016/S0169-1317(01)00039-4
96. Tohdee, K., Kaewsichan, L.: Enhancement of adsorption efficiency of heavy metal Cu (II) and Zn (II) onto cationic surfactant modified bentonite. J. Environ. Chem. Eng. **6**(2), 2821–2828 (2018). https://doi.org/10.1016/j.jece.2018.04.030
97. Bors, J., Dultz, S., Riebe, B.: Organophilic bentonites as adsorbents for radionuclides: I. Adsorption of ionic fission products. Appl. Clay Sci. **16**(1–2), 1–13 (2000). https://doi.org/10.1016/S0169-1317(99)00041-1
98. Yahya, K., Msadok, I., Mlayah, A., Srasra, E., Hamdi, N.: Retention and selectivity of phosphate and fluoride from single and industrial aqueous solutions using purified and surfactant modified Tunisian clay. Desalination **216**, 199–210 (2021). https://doi.org/10.5004/dwt.2021.26814

99. Luo, W., Huang, Q., Zhang, X., Antwi, P., Mu, Y., Zhang, M., Xing, J., Chen, H., Ren, S.: Lanthanum/Gemini surfactant-modified montmorillonite for simultaneous removal of phosphate and nitrate from aqueous solution. JWPE **33**, 101036 (2020). https://doi.org/10.1016/j.jwpe.2019.101036
100. Ma, J., Cui, B., Dai, J., Li, D.: Mechanism of adsorption of anionic dye from aqueous solutions onto organobentonite. J. Hazard. Mater. **186**(2–3), 1758–1765 (2011). https://doi.org/10.1016/j.jhazmat.2010.12.073
101. Fan, H., Zhou, L., Jiang, X., Huang, Q., Lang, W.: Adsorption of Cu^{2+} and methylene blue on dodecyl sulfobetaine surfactant-modified montmorillonite. Appl. Clay Sci. **95**, 150–158 (2014). https://doi.org/10.1016/j.clay.2014.04.001
102. Azejjel, H., Ordax, J.M., Draoui, K., Rodríguez-Cruz, M.S., Sánchez-Martín, M.J.: Effect of cosolvents on the adsorption of ethofumesate by modified Moroccan bentonite and common clay. Appl. Clay Sci. **49**(3), 120–126 (2010). https://doi.org/10.1016/j.clay.2010.04.014
103. Shirzad-Siboni, M., Khataee, A., Hassani, A., Karaca, S.: Preparation, characterization and application of a CTAB-modified nanoclay for the adsorption of an herbicide from aqueous solutions: Kinetic and equilibrium studies. C R Chim. **18**(2), 204–214 (2015). https://doi.org/10.1016/j.crci.2014.06.004
104. Chang, Y., Lv, X., Zha, F., Wang, Y., Lei, Z.: Sorption of p-nitrophenol by anion–cation modified palygorskite. J. Hazard. Mater. **168**(2–3), 826–831 (2009). https://doi.org/10.1016/j.jhazmat.2009.02.105
105. Hernández-Hernández, K.A., Illescas, J., Díaz-Nava, M.d.C., Martínez-Gallegos, S., Muro-Urista, C., Ortega-Aguilar, R.E., Rodríguez-Alba, E., Rivera, E.: Preparation of nanocomposites for the removal of phenolic compounds from aqueous solutions. Appl. Clay Sci. **157**, 212–217 (2018). https://doi.org/10.1016/j.clay.2018.01.020
106. Jarraya, I., Fourmentin, S., Benzina, M., Bouaziz, S.: VOC adsorption on raw and modified clay materials. Chem. Geol. **275**(1), 1–8 (2010). https://doi.org/10.1016/j.chemgeo.2010.04.004
107. Jin, X., Zha, S., Li, S., Chen, Z.: Simultaneous removal of mixed contaminants by organoclays—amoxicillin and Cu (II) from aqueous solution. Appl. Clay Sci. **102**, 196–201 (2014). https://doi.org/10.1016/j.clay.2014.09.040
108. Luo, W., Ouyang, J., Antwi, P., Wu, M., Huang, Z., Qin, W.: Microwave/ultrasound-assisted modification of montmorillonite by conventional and gemini alkyl quaternary ammonium salts for adsorption of chromate and phenol: structure-function relationship. Sci. Total Environ. **655**, 1104–1112 (2019). https://doi.org/10.1016/j.scitotenv.2018.11.329
109. Ma, L., Chen, Q., Zhu, J., Xi, Y., He, H., Zhu, R., Tao, Q., Ayoko, G.A.: Adsorption of phenol and Cu (II) onto cationic and zwitterionic surfactant modified montmorillonite in single and binary systems. J. Chem. Eng. **283**, 880–888 (2016). https://doi.org/10.1016/j.cej.2015.08.009
110. Lee, S.M., Tiwari, D.: Organo-modified sericite in the remediation of an aquatic environment contaminated with As (III) or As (V). Environ. Sci. Pollut. Res. **21**(1), 407–418 (2014). https://doi.org/10.1016/j.clay.2012.02.006
111. Wu, P., Dai, Y., Long, H., Zhu, N., Li, P., Wu, J., Dang, Z.: Characterization of organo-montmorillonites and comparison for Sr (II) removal: equilibrium and kinetic studies. J. Chem. Eng. **191**, 288–296 (2012). https://doi.org/10.1016/j.cej.2012.03.017
112. Gammoudi, S., Frini-Srasra, N., Srasra, E.: Nitrate sorption by organosmectites. Eng. Geol. **124**, 119–129 (2012). https://doi.org/10.1016/j.enggeo.2011.10.009
113. Park, Y., Sun, Z., Ayoko, G.A., Frost, R.L.: Bisphenol A sorption by organo-montmorillonite: Implications for the removal of organic contaminants from water. Chemosphere **107**, 249–256 (2014). https://doi.org/10.1016/j.chemosphere.2013.12.050
114. Wang, G., Zhang, S., Hua, Y., Su, X., Ma, S., Wang, J., Tao, Q., Wang, Y., Komarneni, S.: Phenol and/or Zn^{2+} adsorption by single-or dual-cation organomontmorillonites. Appl. Clay Sci. **140**, 1–9 (2017). https://doi.org/10.1016/j.clay.2017.01.023
115. Nourmoradi, H., Avazpour, M., Ghasemian, N., Heidari, M., Moradnejadi, K., Khodarahmi, F., Javaheri, M., Moghadam, F.M.: Surfactant modified montmorillonite as a low cost adsorbent for 4-chlorophenol: Equilibrium, kinetic and thermodynamic study. J. Taiwan Inst. Chem. Eng. **59**, 244–251 (2016). https://doi.org/10.1016/j.jtice.2015.07.030

116. Zhu, R., Chen, W., Liu, Y., Zhu, J., Ge, F., He, H.: Application of linear free energy relationships to characterizing the sorptive characteristics of organic contaminants on organoclays from water. J. Hazard. Mater. **233–234**, 228–234 (2012). https://doi.org/10.1016/j.jhazmat.2012.07.025
117. Perelomov, L., Mandzhieva, S., Minkina, T., Atroshchenko, Y., Perelomova, I., Bauer, T., Pinsky, D., Barakhov, A.: The synthesis of organoclays based on clay minerals with different structural expansion capacities. Minerals **11**(7), 707 (2021). https://doi.org/10.3390/min11070707
118. Xi, Y., Mallavarapu, M., Naidu, R.: Preparation, characterization of surfactants modified clay minerals and nitrate adsorption. Appl. Clay Sci. **48**(1), 92–96 (2010). https://doi.org/10.1016/j.clay.2009.11.047
119. Nguyen, T.D.C., Dao, T.P., Tran, H.T., Nguyen, D.B., Ahn, D.H.: Synthesis of organoclays and their application for the adsorption of phenolic compounds from aqueous solution. J. Ind. Eng. Chem. **19**(2), 640–644 (2013). https://doi.org/10.1016/j.jiec.2012.09.018
120. Akçay, G., Kılınç, E., Akçay, M.: The equilibrium and kinetics studies of flurbiprofen adsorption onto tetrabutylammonium montmorillonite (TBAM). Colloids Surf, A Physicochem Eng. Asp. **335**(1–3), 189–193 (2009). https://doi.org/10.1016/j.colsurfa.2008.11.009
121. Dos Santos, A., Viante, M.F., Pochapski, D.J., Downs, A.J., Almeida, C.A.P.: Enhanced removal of p-nitrophenol from aqueous media by montmorillonite clay modified with a cationic surfactant. J. Hazard. Mater. **355**, 136–144 (2018). https://doi.org/10.1016/j.jhazmat.2018.02.041
122. Zhang, Q., Meng, Z., Zhang, Y., Lv, G., Lv, F., Wu, L.: Modification of a Na-montmorillonite with quaternary ammonium salts and its application for organics removal from TNT red water. Water Sci. Technol. **69**(9), 1798–1804 (2014). https://doi.org/10.2166/wst.2014.039
123. Nafees, M., Waseem, A.: Organoclays as sorbent material for phenolic compounds: a review. Clean (Weinh) **42**(11), 1500–1508 (2014). https://doi.org/10.1002/clen.201300312
124. Sarkar, B., Xi, Y., Megharaj, M., Krishnamurti, G.S.R., Bowman, M., Rose, H., Naidu, R.: Bioreactive organoclay: a new technology for environmental remediation. Crit. Rev. Environ. Sci. Technol. **42**(5), 435–488 (2012). https://doi.org/10.1080/10643389.2010.518524
125. Sarkar, B., Megharaj, M., Xi, Y., Naidu, R.: Structural characterisation of Arquad® 2HT-75 organobentonites: surface charge characteristics and environmental application. J. Hazard. Mater. **195**, 155–161 (2011). https://doi.org/10.1016/j.jhazmat.2011.08.016
126. Shen, Y.H.: Removal of dissolved organic matter from water by adsorption-flocculation using organobentonite. Environ. Technol. **23**(5), 553–560 (2002). https://doi.org/10.1080/09593332308618391
127. Luo, Z., Gao, M., Yang, S., Yang, Q.: Adsorption of phenols on reduced-charge montmorillonites modified by bispyridinium dibromides: mechanism, kinetics and thermodynamics studies. Colloids Surf, A Physicochem. Eng. Asp. **482**, 222–230 (2015). https://doi.org/10.1016/j.colsurfa.2015.05.014
128. Lin, S.-H., Juang, R.-S.: Heavy metal removal from water by sorption using surfactant-modified montmorillonite. J. Hazard. Mater. **92**(3), 315–326 (2002). https://doi.org/10.1016/S0304-3894(02)00026-2
129. Su, J., Huang, H.-G., Jin, X.-Y., Lu, X.-Q., Chen, Z.-L.: Synthesis, characterization and kinetic of a surfactant-modified bentonite used to remove As (III) and As (V) from aqueous solution. J. Hazard. Mater. **185**(1), 63–70 (2011). https://doi.org/10.1016/j.jhazmat.2010.08.122
130. Leyva-Ramos, R., Jacobo-Azuara, A., Torres-Rivera, O.L., Guerrero-Coronado, R.M., Berber-Mendoza, M.S., Alonso-Davila, P.: Adsorption of chromium (VI) from water solution onto organobentonite. J. Environ. Eng. Manag. **18**(5), 311–317 (2008)
131. Majdan, M., Maryuk, O., Pikus, S., Olszewska, E., Kwiatkowski, R., Skrzypek, H.: Equilibrium, FTIR, scanning electron microscopy and small wide angle X-ray scattering studies of chromates adsorption on modified bentonite. J. Mol. Struct. **740**(1–3), 203–211 (2005). https://doi.org/10.1016/j.molstruc.2005.01.044
132. Rathnayake, S.I., Xi, Y., Frost, R.L., Ayoko, G.A.: Structural and thermal properties of inorganic–organic montmorillonite: Implications for their potential environmental applications. J. Colloid Interf. Sci. **459**, 17–28 (2015). https://doi.org/10.1016/j.jcis.2015.07.071

Surfactant-Modified Clay Composites: Water Treatment Applications

M. D. R. Perera, R. A. L. R. Amarasena, W. M. A. T. Bandara, R. Weerasooriya, and L. Jayarathna

Abstract The accumulation of various contaminants in water has become a threatening environmental issue, affecting all living creatures. Owing to this fact, mitigating water contamination problems by improving existing technologies and developing potential strategies has become an emerging area of research. Among several approaches for water treatment, adsorption has been attractive since it has unique advantages due to the use of natural and synthetic materials. As a natural adsorbent material, clay minerals are considered superior materials owing to their wide availability, low cost, excellent adsorption performance and cation exchangeability. To enhance the surface properties toward the removal of water pollutants, natural clays are subjected to various modifications. The surfactant-modified clay composites can remove a variety of pollutants than other composites due to the sorption of surfactant onto the external surface and interlayer spacing of clay minerals. This chapter encloses the application of surfactant-modified clay towards the removal of pollutants from water.

Keywords Clay composite · Surfactant · Adsorption · Ion exchange · Water treatment

1 Overview

Safe and clean water is one of the most pivotal requirements for all living creatures and ecosystems on Earth. However, the tremendous increase in the worldwide population and growing industrialization have created a higher demand for available freshwater, while resulting in large amounts of wastewater globally. Direct discharge of polluted water containing a number of complex chemical wastes such as industrial wastes,

---

M. D. R. Perera · R. A. L. R. Amarasena · R. Weerasooriya · L. Jayarathna (✉)
National Institute of Fundamental Studies (NIFS), Hantana, Kandy, Sri Lanka
e-mail: lakmal.ja@nifs.ac.lk

W. M. A. T. Bandara
Department of Chemistry, University of Peradeniya, Kandy, Sri Lanka

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_11

sewage, agricultural wastes, radioactive waste, pesticides, and chemical fertilizers into the natural water resources has created an enormous environmental issue in the present world. This fact has led a considerable portion of the world's population into a water-stressed condition, making the treatment of contaminated water, a dire necessity to fulfill the fundamental requirements of good-quality water [2].

Scores of technologies and methodologies have been practiced so far to remediate water contamination matter and these include, membrane filtration, chemical precipitation, reverse osmosis, electrodialysis, and adsorption [23]. Due to the significant advantages like flexibility, low cost, profitability, design simplicity, and avoiding secondary contaminant formation, the adsorption technique has obtained much interest compared with the other remediation techniques. It is known as an effective process to remove any cationic, anionic, or organic contaminants from one phase, and uptake those contaminants on the external surface by several mechanisms (will be discussed later in this chapter). The technique of adsorption is classified as chemical or physical. The former is due to the electron exchange and the pollutant (adsorbate) bounded to the surface by a chemical bonding. In the latter process, physical forces such as Van der Waals forces, hydrogen bonding, polarity, and dipole–dipole interactions function to attach waste materials to the adsorbent surface [12]. So far, several adsorbents have been reported for pollutant removal including activated carbon, chitosan, zeolites, clay, materials like resins as artificial adsorbents, and biomass as bio-adsorbents [4].

Clay minerals are one of the famous adsorbents which are used commonly in wastewater treatment due to their low cost, availability, high chemical and mechanical stability, internal and external layers with high adsorption capacity, porous structure with high surface area, etc. These are phyllosilicate minerals and have layered units by one or two tetrahedral silica sheets attached to an octahedral aluminum sheet, which are bonded in 2:1 (T-O-T) and 1:1 (T-O) ratios. The tetrahedral silica sheet is made of $Si_2O_6(OH)_4$ units and the octahedral aluminum sheet is composed of $Al_2(OH)_6$ units. Natural clay materials such as kaolinite (1:1 layer), halloysite (1:1 tube), bentonite/montmorillonite/smectite (2:1 layer), palygorskite/attapulgite, sepiolite (2:1 layer-chain), illite; some of the most abundant clays that are used in water treatment applications [11, 37]. The chemical nature and pore structure generally determine the sorption ability of clay. Clay minerals have their Cation Exchange Capacity (CEC) since the negative charge is available on the unmodified clay surfaces which can be balanced by counter cation. Therefore, most of the time unmodified clays are suitable for the removal of cationic pollutants via this counter-ion exchange. As it depends on the protonation of hydroxyl groups on the surfaces of metal oxides and the edges of silicate clays, which is significantly influenced by the parameters of pH and temperature, the anion exchange capacity (AEC) of clay minerals varies from the cation exchange capacity (CEC) [14]. It is noted that swelling of clay can reduce the hydraulic conductivity, and then pollutants cannot adsorb into the clay easily. As a result, metal ions cannot be effectively removed from the aqueous solution by natural clay [33]. Due to this fact, the modification of natural clay minerals is a necessity to enhance their pollutant removal performance.

Choosing an appropriate modifier is a key factor to obtain modified clay adsorbents with higher efficiency. Fundamentally, the modification alters the properties of natural clay minerals by enhancing their specific surface area, pore volume, and the number of surface acid sites. There are several modification techniques such as thermal treatment, acid washing, metal oxide pillaring, organic modification based on the characteristics of structure and surface charge [37]. Organic modification is introducing organic molecules to the mineral structure to enhance its efficiency in removing pollutants. The introduction of surfactants, polymers, and organic chelating agents with a positive charge is favored for the removal of anionic contaminants through various physical adsorption mechanisms such as electrostatic attraction, anion exchange. These modified clays are known as organoclays which are used in many water purification applications [20].

Among several modification techniques, surfactant modification is known as a convenient and promising method to enhance the clay mineral properties towards contaminant removal. Generally, surfactant modification is done by using surfactants that provide polar hydrophilic groups and non-polar lipophilic groups for clay functionalization. The fundamental advantage of this technique is the ability to achieve better dispersion stabilization. Since clay minerals have amphiphilic characteristics, surfactants get adsorbed at diverse interfaces and surfaces of the clay particles and function to maintain hydrophobic–hydrophilic balances, resulting in the stabilization of dispersions. Fundamentally, surfactant modification of clays is described according to mechanisms such as (1) ion exchange due to the replacement of counter ions on clay from charged surfactant ions, adsorption by π electrons polarization due to strongly positive clay sites and the electron-rich aromatic nuclei of a surfactant, (2) ion paring by surfactant ion adsorption onto the oppositely charged adsorbent sites that are unoccupied by counter ions, (3) hydrophobic bonding, (4) adsorption by dispersion forces. Quaternary ammonium cation surfactants are the extensively used type of surfactant in clay modification for the recovery of organic and inorganic water contaminants. In addition to the cationic surfactants, clays have been modified by anionic, non-ionic, and zwitterionic surfactants for the same purpose. Furthermore, mixed surfactants also have been employed in water remediation applications since they have shown more complex behavior relative to single surfactants. However, the behavior of these surfactant-modified clay minerals in pollutant removal processes is highly dependent on surfactant type, their concentration, and the other factors pH, temperature, adsorbent dosage, and contact time. Therefore, the optimization of operating conditions towards the best adsorption performance is identified as a key research area in the water treatment research field and numerous efforts have been made so far in this regard.

This chapter is to provide adequate information about the ability of surfactant-modified clay composites to enhance water treatment performance. Further, a comprehensive analysis of the effects of operating conditions on the adsorption performance of surfactant-modified clay composites will be discussed. Moreover, the mechanisms undergone during the pollutant removal process will be discussed.

2 Role of Surfactant-Modified Clay Composites in Water Treatment

2.1 Organic Pollutants Removal by Surfactant-Modified Clays

Emerging organic pollutants enter into the water through uncontrolled anthropogenic activities recognized as a critical environmental issue at present. A wide range of these organic contaminants such as dyes, pharmaceuticals, pesticides, humic substances, microplastics, phenolic compounds found in water is known to have a direct effect on human health and the entire ecosystem. Therefore, the removal of these contaminants from polluted water has proved a complicated challenge for the scientific community. In this section, the role of surfactant-modified clay composites in organic pollutant removal in water based on their treatment performance will be discussed.

2.1.1 Organic Dyes

Dyes are one of the complex classes of organic compounds that consist of functional groups such as auxochromes (N_2, NO, and NO_2) and chromophoric groups (NR_2, NHR, NH_2, COOH, and OH). Due to the higher toxicity of these compounds towards the environment and mankind, treating the polluted water with dye contaminants has been tried so far to get rid of these contaminants. Broadly, on the basis of their chemical functionality, dyes are classified as acid dyes, basic dyes, direct dyes, disperse dyes, and reactive dyes which all have severe health effects. Acid dyes are also known as anionic dyes and acid red 57, acid blue 2, orange (I, II), and methyl orange, are common examples. Basic dyes such as basic red 46, basic yellow 28, methylene blue crystal violet, and malachite green are soluble in water and have the ability to yield colored cations and are also known as cationic dyes. Including cationic and anionic dyes, all the other dye types have a considerable effect on water contamination and remediation efforts have been reported so far through different approaches [12].

Among the various toxic cationic dyes, methylene blue (MB) is a dye that is difficult to degrade due to its light stability and oxidation reactions. More often it employs as a model dye of organic contaminant [29]. There are several research efforts have been taken to remove methylene blue from water by adsorption technique. In many efforts, cationic surfactant-modified clay minerals are employed in the removal of this kind of basic dye. With the purpose of methylene blue removal, brown clay (BC) has been modified with didodecyldimethylammonium bromide (DDAB) to produce a sorbent (DDAB-BC). This modification has been done by cation exchange of the DDAB moiety with positive ions existing inside the BC interlayer spaces. In this study, batch sorption investigations have revealed that the modified material has a superior removal efficiency ($\sim$98%) towards methylene blue and sorption capacity ($\sim$164 mg/g) at optimum adsorption conditions of pH (7), dye concentration (100 mg/L), and temperature (55 °C) [22]. Another reported study on MB removal has been employed to comparatively investigate several clay-based materials that are modified with surfactants as well as alginate, iron oxide nanoparticles, and sodium carbonate. The surfactant that was used in the study is Lansperse LT87, which has powerful dispersion properties, minimal ecotoxicity, lack of VOC emission, and good steric stabilization. This surfactant-modified composite displayed a removal efficiency of 90%, however almost similar to that of the other materials [21].

A study has reported the modification of bentonite clay with two structurally different surfactants (hexadecyltrimethylammonium bromide (HDTMAB) and benzyldimethylhexadecylammonium chloride (BDHAC)) having the same carbon chain length. The composite prepared using HDTMAB (H-Bt) showed the maximum adsorption capacity of 114.3 mg/g for orange G (OG) dye which is an anionic dye, which was 1.74 times higher than that of the composite prepared using BDHAC (B-Bt). However, in a mixed dye system of cationic (methylene blue) and anionic dye (orange G) molecules in water, H-Bt showed a higher removal of the cationic dye (i.e., methylene blue) than the anionic dye molecules. However, for the OG dye, both composites showed a similar removal tendency. Based on this, it can be concluded that both of these surfactant-modified composites are more efficient at adsorbing anionic dye pollutants from water than cationic ones. This is due to the tendency to electrostatically adsorb anions since both composites have high surface charges (+47.8 mV for H-Bt, +54.21 mV for B-Bt) [6].

However, being almost similar to the basic (anionic) dyes, cationic surfactants are often employed in clay modification for cationic dye removal too. For the removal study on cationic dye rhodamine B, a sensitive and fast solid phase extraction technique has been reported based on the liquid chromatography-electrospray ionization tandem mass spectrometry method. This is based on the Rhodamine B extraction by cetyltrimethylammonium bromide (cationic surfactant) intercalated montmorillonite (clay k10) followed by elution. Even at trace levels, this modified clay composite resulted in a highly efficient extraction performance. Further, the clear noticeable physical changes in the color of the composite after the solution passage through the CTAB-MMT column indicate the proper dye adsorption by the material [3]. However, there exists some reported literature that anionic dyes are also used in clay modification for the removal of cationic dyes like rhodamine B.

The reported studies show that the application of anionic surfactants was also reported for dye removal. However, when compared with cationic ones, anionic surfactants have a small tendency to intercalate within clay mineral interlamellar spaces. Further, it was confirmed that anionic surfactants cannot intercalate solely within interlamellar spaces of clay minerals like montmorillonite (Mt) unless via interaction with cationic surfactants. Based on this fact, a new class of montmorillonite clay modified with both an anionic surfactant (sodium eicosenoate–SEIA) and a cationic surfactant (cetyltrimethylammonium chloride–CTMAC) has been synthesized along with magnetic nanoparticles. This composite adsorbent material was applied in methylene blue removal from contaminated water. Through the clay mineral modification with cationic plus anionic surfactants, carbonic contents and the hydrophobic property of the clay mineral were intensively increased and the nanocomposite of Fe3O4-CTMAC/SEIAMt showed the best adsorption capacity [29].

Apart from basic dyes like methylene blue, reactive dyes are also anionic in nature. A recent research effort has been taken to remove reactive yellow 160 dye (RY160) with zwitterionic surfactant-modified natural clay minerals. Using cocamidopropyl betaine (CAPB) as the surfactant, clays were modified at different conditions (CAPB concentration, reaction temperature, and reaction time). According to the results of the study, it has clearly concluded that the unmodified natural clay adsorbed a very less amount (2 mg/g) of RY160. In contrast, the modified natural clay by CAPB has shown a great adsorption efficiency enhancement (12 mg/g). During the surfactant modification, each inorganic cation of natural clay is repealed by an amide group and a carboxylate group of CAPB, and therefore, the potential sites of adsorption are increased. When the observations are correlated to the results of textural investigations, it is very much clear that CPAB modification plays a major role in the RY160 adsorption process [1].

2.1.2 Hydrocarbons

Monocyclic Aromatic Hydrocarbons

BTEX (Benzene, Toluene, Ethylbenzene, Xylene)

Monocyclic aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, and xylene (BTEX) are hazardous organic contaminants that are frequently added into groundwater by industrial sources like particular gasoline fraction and crude oil. According to recent reports, the BTEX concentrations in water have reached a considerably higher level, threatening the overall ecosystem due to their severe carcinogenic behavior as well as other health issues such as respiratory and cardiovascular illnesses, neurological impairment, and acute myelogenous leukemia. According to the World Health Organization (WHO), the maximum benzene, toluene, and xylene concentrations in drinking water should be 0.01, 0.5, and 0.7 mg/l, respectively. Therefore, the BTEX removal from contaminated water is a highly essential task and several research efforts have been taken so far in different approaches to reach this objective. Bentonite clay, in its natural and surfactant-modified states, has been used as an adsorbent to study the multi-component adsorption of benzene, toluene, ethylbenzene, and xylene (BTEX) from aqueous solutions. Trimethylphenyl Ammonium (TMPA) and Hexadecyltrimethyl Ammonium (HDTMA) had been used in this study as surfactants to modify Nigerian bentonite clay and batch adsorption experiments have been conducted. This modification has led to an increment in the surface area of TMPA and HDTMA-modified bentonite from 512.6 m^2/g and 327 m^2/g, respectively, implying the existence of micropores in the interlayer between organic cations. Further, the modification has increased the cation exchange capacity (CEC) of the adsorbent materials. Moreover, the long-chain alkyl ammonium ions have the ability to create a favorable interlayer microenvironment for organic molecule partitioning. Due to this fact, the charge density of the clay layer and the size of the alkyl chain are considered the responsible components for the CEC increase after modification, which directly accounts for the increased absorbance performance towards BTEX [27]. Another similar study has reported on investigating the BTEX removal from produced water using CTAB surfactant-modified bentonite clay. “Produced water” is a byproduct of almost all gas and oil extraction and it can cause pollution of surface water and groundwater it contains benzene, toluene, ethylbenzene, and xylene (BTEX). In this particular study, CTAB-modified bentonite has shown a 95.6% capability of adsorbing BTEX contaminants from produced water respectively in the order of ethylbenzene, xylene, toluene, and benzene. This adsorption difference has been attributed to the relative polarity and the molecular size of compounds. Indeed, benzene and ethylbenzene offered the lowest and highest adsorption by CTAB-modified clay because of having smaller and larger molecules with the size of 6.6 Å and 9.5 Å, respectively [25].

Generally, an adsorbent with a higher number of micropores and a large specific surface area (S_{BET}) exhibits excellent adsorption performance towards volatile organic contaminants like benzene. It has been reported that montmorillonite (Mt) clay modified with small surfactants like tetramethylammonium bromide (TMAB) has a larger value of S_{BET} and more interlayer micropores compared to Mt modified with larger surfactants and may lead to excellent adsorption performance towards volatile organic carbons (VOCs). However, several factors like the charge density of clay mineral and the size of the surfactant have an influence on the microstructure of the adsorbents modified with small surfactants and would therefore have an impact on the VOC adsorption process. According to the reported literature, the charge density of Mt clay has an influence on the VOCs adsorption behavior of TMAB-modified Mt by affecting the packing density of surfactant (TMA^+) cations and the micropores formation. Furthermore, the adsorption behavior of Mt modified with small surfactants is also affected by surfactant dosage, which can control the microstructure of the resulting adsorbent [8].

Phenol

Organic pollutants such as phenol have the ability to stay chemically stable against conventional biodegradation and therefore need some advanced remediation techniques. Complex contaminants such as personal care waste and/or pharmaceutical release rates are increased recently and they show resistance to traditional treatment applications due to their trace concentrations. Pillared clays (a modified type of raw with increased porosity and permanent interlayered spaces resulting from the addition of several pillars into the parent clay structure) have been used as adsorbents to remove pollutants such as oxyanions and heavy metal cations; however, they are unable to remove hydrophobic organic contaminants due to their extreme hydrophobic properties and polarity. Organic surfactant modification of these pillared clays has the ability to result in inorganic-organo clays which are compatible with both organophilic and hydrophilic compounds and have the ability to remove a wide range of inorganic and organic pollutants. Cationic surfactants such as cetyltrimethylammonium chloride (CTAC) and cetyltrimethylammonium bromide (CTAB) are the commonly used surfactants in pillared clay modification. The surfactant modification has the ability to intensively decrease the specific surface area, due to the introduction of surfactant molecules between the pillared clay layers and filling empty spaces. Further, the amount of the surfactant added and the surfactant structure (type) has a direct effect on the surfactant arrangement between the layers of the pillared clay. The optimum organic cation (surfactant) amount for the modification of pillared clays is generally equal to the cation exchange capacity (CEC) of the starting clay material. Montmorillonite clay modified with cetyltrimethylammonium bromide (CTAB) has been applied as an effective adsorbent to remove organic pollutants such as phenol, 3-Chlorophenol, and 3,5-Dichlorophenol [24]. In addition to pillared clay materials, clay minerals like attapulgite (ATP) have been used in phenol removal from wastewater. For the improvement of the phenol removal ability of attapulgite (ATP), a reported study has synthesized a cationic surfactant (Gemini) having double cation active sites. It was used for the modification of ATP combined with the surfactant cetyltrimethylammonium bromide (CTAB) and a new type of adsorbent (G-ATP) was obtained. This adsorbent material shows better dispersibility and also has increased active cationic groups on the surface. Further, the material is provided with an enhanced surface hydrophobicity due to the replacement of the adsorbed water on the surface of ATP by the cationic surfactant molecules. Therefore, the positively charged modified ATP (G-ATP), having a hydrophobic surface has the ability to adsorb and remove phenol through electrostatic interaction in addition to the π–π interaction between the adsorbent surface and the benzene ring in the phenol structure. The Gemini-modified ATP has shown a better phenol adsorption capacity than that of pure ATP adsorbents. Further, the reusability measurements have revealed that G-ATP has a good regeneration performance too [34].

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are of major research concern owing to their carcinogenic effects and widespread presence in the environment. This group of organic compounds consists of two or more aromatic rings which are fused with each other and these originated from both anthropogenic and natural sources. Several clay minerals including bentonite, have been used as adsorbents for PAHs with modifications by surfactants. There are more than 100 PAHs have been identified so far, but only 16 PAHs are considered priority contaminants by the US EPA and EU based on their potentially carcinogenic, mutagenic, and highly toxic nature. A study has been reported on investigating the adsorption capacity of montmorillonite (Mt) clay, synthetic (Na-Mica-4), and surfactant (octadecylamine and octadecyltrimethylamine) modified clay minerals towards the prioritized PAHs removal. The materials were very much effective in PAH adsorption, with almost 100% adsorption percentage, in particular, those using Mt. However, unmodified clay materials have shown a better adsorption capacity than the modified derivatives, which indicates the possibility of PAHs adsorption in the surface part as well as in the interlayer [31]. Moreover, a reported study has revealed that bentonite clay modified with sodium dodecyl sulfate has the ability to adsorb and remove acenaphthylene, acenaphthene, phenanthrene, anthracene, and naphthalene from water up to 76%. Furthermore, lightweight expanded clay aggregates (LECAs) modified with stearyldimethyl benzyl ammonium chloride (SDBAC) have also been shown their functionality as adsorbents for the removal of PAHs such as fluoranthene, phenanthrene, benzo[a]anthracene, fluorene, and pyrene achieving removal rates of up to 98%, from their initial concentrations of 6–80 g/dm^3 [9].

2.2 Inorganic Pollutants Removal by Surfactant-Modified Clays

Inorganic substances should be present in drinking water but if their permissibility level exceeds, they become harmful substances to the environment and the human body. Those are mainly eluting from inorganic chemical manufacturing industries, pharmaceutical industries, bulk petrochemical plants, agricultural areas, and all other industries that are using inorganic chemicals in their processes. Inorganic pollutants such as heavy metals, metallic salts and non-metallic salts, halogens, acids, and bases are toxic, mutagenic, carcinogenic, and mostly non-biodegradable. Because of the non-degradable, stable behavior of the inorganic pollutants in water, it can persist for longer periods and cause further deterioration of the water quality. Inorganic pollutants are available in water systems in form of elements and in combination with other compounds [35]. In this section, inorganic pollutants removal from surfactant-modified clay will be discussed under two sub-categories.

2.2.1 Anionic Inorganic Pollutants Removal by Surfactant-Modified Clays

Anions are one of the major classes of water contaminants responsible for some environmental conditions. The most common anions found in wastewater are metallic oxyanions such as (AsO_2^-, AsO_4^{3-}, $H_2AsO_4^-$ and $HCrO_4^-$), halides, sulfides, cyanide, nitrates, and phosphate [18]. The modified clay mineral surface needs to have active sites that are positively charged or the weakly held counter ions of the surfactant have to be replaced by more strongly held adsorbate counter ions, in order to proper adsorption of anions [13]. It has been reported that some specific cationic surfactants have provided such a proper modified surfaces for anion adsorption. Most studies based on surfactant-modified clay have focused to remove anions by cationic surfactants such as hexadecyltrimethylammonium bromide (HDTMAB) modified montmorillonite (Montmorillonite), organo-bentonite, alkyl quaternary ammonium-modified montmorillonite, cationic Gemini surfactants modified montmorillonite

[15]. Alkyl ammonium-modified clay minerals show unique adsorptive properties and hence this modification is studied by most researchers. A previous study on nitrate removal from water by HDTMA-modified montmorillonite (Montmorillonite) clay has concluded the ability of this modified clay for nitrate removal with a great removal efficiency of 14.76 mg/g [14]. Further, according to the same study, nitrates removals with Montmorillonite are higher than those with modified kaolinite with the same surfactant due to the high interlayer space and surface area of montmorillonite than kaolinite suggesting the better suitability of HDTMA-modified montmorillonite. The cation exchange capacity of these clays with surfactants is related to the morphological structure of clay minerals so the specific surface area of clays will decrease after modification. But Montmorillonite can provide more positive active sites on the adsorbent surface for nitrate adsorption [14]. Another study shows that chromate removal from HDTMA modified kaolinite, Montmorillonite, and pillared Montmorillonite and HDTMA modified montmorillonite has shown relatively higher adsorption [13]. Moreover, cationic surfactants are known to have an ability to convert the clay surface potentials from negative to positive, that enhance the anionic contaminant removal. This fact has confirmed by a reported study where, montmorillonite has shown its zeta potention change from negative to positive after modification with cetylpyridinium chloride (CPC). Further, the modified material has shown an excellent removal behavior of anionic hexavalent chromium (Cr(VI)) [32].

Several studies have synthesized novel organo-clay composites by modification with both amphoteric and another type of surfactant to have great adsorption capacity towards various pollutants in water. Amphoteric surfactants are non-toxic, have a stable eco-friendly chemical structure, and are effective in clay surface fabrication for pollutant removal from water. The amphoteric surfactants have the ability to modify the clay surface by an organic phase due to their hydrophobic chain, and therefore the negative charge can get reduced. The adsorption of anionic pollutants such as chromate and dichromate onto both amphoteric-cationic surfactant-modified clay surfaces shows significantly higher adsorption behavior [30]. Tungstate removal has been studied with three cationic Gemini surfactants with different alkyl chain lengths applied to Montmorillonite. Here longer chain has shown low adsorption because specific surfaces of clay decrease with increasing chain length [36]. Moreover, positively charged head groups in Gemini surfactants ($-R_4N^+$) are making non-specific adsorption sites on the clay surface hence affinity of anions to adsorption sites obeys the Hofmeister order which is $PO_4^{3-} < CO_3^{2-} < SO_4^{2-} << Cl^- < Br^- < NO_3^-$. Removal of co-existing other anions can alter the adsorption of anions. Most of the time chloride, carbonate, and sulfates coexist with phosphate and nitrates. Sulfate cannot exchange bromide but nitrate uptake can increase in the presence of sulfate due to the difference in ion size and high hydration energy of sulfate which expose more adsorption sites on the modified clay [16].

Most toxic metals such as arsenic available in groundwater and are commonly available in arsenite and arsenate forms [20]. Modified a smectite sample using three organic agents, namely hexadecyl trimethylammonium (HDTMA), chitosan, and citric acid [20] has been used to study arsenic removal. It has been found that anionic heavy metals such as As(V) ions actively adsorb into 1:1 layered clay as kaolin than

2:1 layered Montmorillonite and illite [18]. For arsenic removal organically modified clay mineral is used by many researchers. Here cationic surfactants are used for the modification and it undergoes ion exchange with Na^+, Ca^{2+}, K^+, and Mg^{2+} in the clay interlayer. So that the net surface charge becomes negative to positive [28].

2.2.2 Cationic Inorganic Pollutants Removal by Surfactant-Modified Clays

Ions with positive charge pollutants in water are mainly can be discussed under heavy metal ions and alkali metal ions. Heavy metals are major cationic pollutants in water that should be removed since their high toxicity to human health and the imbalance of nature activities. Heavy metals are released from various industries such as the metal and electroplating industry, metallurgical industry, chemical manufacturing, and battery manufacturing as well as from tannery operations, mine drainage, leachates from landfills, etc. Moreover, due to hazardous waste sites, groundwater contaminates with heavy metals. Some heavy metals are available in oxy-anionic forms such as chromate, arsenate. Most of the heavy metals are in cationic form. Heavy metals such as Ag(I), Hg(II), Cd(II), As(III), Cu(II), Pb(II), Ni(II), and Cr(VI) are markedly toxic even at low concentrations. The World Health Organization (WHO) has entitled more elements such as heavy metals and risk metals for public health.

To remove cationic inorganic pollutants using clay minerals there should be negatively charged sites for adsorption or weakly head counter cation for ion exchange. Due to the large number of exposed hydroxyl groups on their surfaces, clay minerals have a considerable capacity for adsorbing heavy metal ions. These groups are made up of structural hydroxyl groups and silanol groups that are coordinated by metal ions produced by broken bonds at the edges of layered crystal structures (e.g., the hydroxy aluminum surface in kaolinite crystals). Certain metal ions have different adsorption selectivity depending on their hydration, radius, and valence. In most cases, the homomorphic substitution of positive cations in the clay mineral interlayers achieves the charge balance. As a result, ion exchange removes the target ions from the metal ion solution when an adsorbent is added. Meanwhile, the optimal adsorption ability is determined by the properties of clay minerals, which include tiny particle size, big surface area, and many structural pores [18].

Cationic Inorganic Pollutant Removal by Anionic Surfactant-Modified Clay

Most of the previous studies on cations removal using surfactants-modified clays have used anionic surfactants such as sodium dodecyl sulfate SDS since they can enhance adsorption capacity towards cations [32]. Although clays have a negative charge on the clay surface, anionic-modified clay is used to remove cationic pollutants more than natural clays of its weak binding strength. Basically, surface-cation complex formation has been attributed to the metal cation sorption on clay materials modified with anionic surfactants [17]. It was reported that this anionic surfactant binds irreversibly to the interlayer of the base clay [17]. Cu^{2+} and Zn^{2+} sorption into anionic surfactant (SDS) modified Montmorillonite has been studied by [15]. The study has reported the ability of surfactant to penetrate the clay's interlamellar area by the clay sheets expanding along the c-axis. The negative charge at the clay surface appears to increase when SDS is grafted to the clay interlayer and will continue to grow with rising pH levels. Although raw montmorillonite weakly bonds to metal cations, it has two different types of acidic groups (XNa and SOH) and exists as a negatively charged particle in aqueous solutions. After SDS modification, most clay surface is intercalated with SDS (RSO_3Na) [15]. In addition to the above facts, into the clays such as bentonite that are swelling in nature large anionic species such as SDS can easily enter and become fixed strongly in the interlayer region. Moreover, clays such as montmorillonite and hectorite composed of 2:1 layers known to have a higher adsorption capacity than clays composed of 1:1 layers towards heavy metals. This has been attributed to their enhanced surface charge with the diffusion of isomorphic substitution. However, Kaolinite which is a 1:1 layered clay has slight isomorphic substitution and hence, weakly adsorbs heavy metals [18].

Cationic Inorganic Pollutant Removal by Cationic Surfactant-Modified Clay

Although anionic surfactants-modified clay are mostly employed in cationic inorganic pollutant removal, there are several reported studies on cationic contaminant removal by cationic surfactant-modified clay adsorbents. A previous study has reported adsorption capacity of Cr(VI) aqueous solution to the cationic surfactant, cetyltrimethylammonium bromide (CTAB)-modified kaolinite (CTAB–kaolinite) is 22.72 mg/g and shows 100% Cr(VI) removal at adsorption equilibrium (time = 180 min, 100 mg CTAB-kaolin, 10 ppm/100 ml) [5]. It has been reported that modification with cetyltrimethylammonium (CTAB) can enhance the adsorption performance of montmorillonite and illite clay [5]. Cationic Gemini surfactant-modified clay has high efficiency towards heavy metal adsorption. The differences in adsorption sites determined the adsorption efficiency of the metal adsorption system [18].

Another study tried to remove Cu^{2+} and Zn^{2+} using bentonite clay modified with Bencylhexadecyldimethyl ammonium chloride, BCDMACl cationic surfactant. It has been suggested that exchangeable cations would be substituted by BCDMACl micelle cations that intercalated into the bentonite's interlayers. As a result, the functional groups of natural bentonites were altered to cationic surfactants, which dominated the adsorption of heavy metal ions and prevented bentonite from swelling. Intercalating into the interlayers, the ammonium cation of BCDMACl micelles substituted the exchangeable cations (Ca^{2+} and Na^{+} in the interlayer) and Mg^{2+} for Al^{3+} in the central octahedral layer [33]. This study has reported that modified bentonite had around 43% removal efficiency with high adsorption capacity than natural bentonite [33]. In addition to cationic and anionic surfactants, amphoteric surfactants which are surface-active compounds with both alkaline and acidic properties have also been employed in cationic contaminant removal. A study has reported that amphoteric surfactant modified magnetic bentonite clay on removing Cd(II) has shown a higher adsorption when compared with bentonite modified with other type of surfactants such as cationic and anionic [30].

3 Factors Affecting Absorbance Performance

3.1 Clay Composite Dosage

Clay composite dosage is an important parameter because it determines the adsorption capacity at a specific initial concentration of pollutants in the water. When increasing the dosage adsorption also increases due to the enhancement of active sites and the easy penetration of ions into active sites [32]. However, in some studies when increasing the weight of clay metal sorption onto modified clay has decreased because sometimes water swelling is easier in the case of few amounts of clay. This observation has been reported in a study that tried to remove Zn^{2+} and Cu^{2+} using SDS-modified Montmorillonite clay [15].

The removal of Cr(VI) increases with increasing CTAB-Kaolin dosage and results show 99% removal efficiency when 100 mg of modified clay is added to 100 ml of 100 ppm chromium solution [5]. In another study, arsenic elimination increases with dosage, peaking at 0.2 g/100 mL after reaching 0.05 g/100 mL. At dosages greater than 0.2 g/100 mL, the adsorption efficiency remained nearly constant, indicating that the adsorbent had achieved its maximal sorption capacity [19].

3.2 Solution pH and Point of Zero-Charge of the Clay

The solution pH affects the surface charge and functional group condition in adsorbents as well as contaminants in the solution. Therefore, the adsorption capacity also depends on the pH [37]. At low pH, hydrogen cations compete with other metal cations in the aqueous solution to get adsorb onto the clay surface. Also, they alter the oxidation state of some metal ions and the surface charge of modified clay and hence adsorption interaction. Therefore, metal ions removal at low pH is less than the optimal removal value [32]. The surface charge of the surfactant can be measured by evaluating the point of zero charges (pHpzc). The point of zero charges (pHpzc) value is an important value that gives a better understanding of the adsorption mechanism. pHpzc is the point where the adsorbent surface has no charge. At a high pH than pHpzc, the surface carries a negative charge and prefers to adsorb cations and at low pH then pHpzc carries a positive charge then favors adsorbing anions [26]. In a reported study on arsenic removal by surfactant-modified clay adsorbents, it has been clearly reported that moderated pH range ($pH = 4–8$) can provide an environment for maximum adsorption. This is because, at moderate pH, there is low charge density on the surface of the adsorbent which facilitates the Van der Waal attractive forces resulting in optimum uptake of As(III) [28]. Although cations like As(III) prefer moderate pH, the maximal removal of Cr(VI) using CTAB-Kaolin is high at low pH values (pH 2). The solution pH is less than pHpzc of modified kaolin, the surface becomes positively charged and attracts CrO_4^{2-} anions. When pH increases, removal efficiency decreased since the surface charge is negative at high pH [5]. In contrast, when adsorbing Cu^{2+} cations into SDS-modified clay, the sorption increases with increasing the pH as the surface becomes more negative. Here when pH is low as described above metal cations compete with hydrogen ions to get adsorbed onto modified clay [15]. In Cu and Zn removal studies using modified clay, adsorption of both metals increases with pH within the range of 3–5. But a remarkable removal of both ions has been observed with the maximal capacity of metal concentration at the solution pH 7–11 (more than 95%). This is due to the precipitation of Cu^{2+} and Zn^{2+} to $Cu(OH)_2$ and $Zn(OH)_2$ in an alkaline solution. Therefore, the optimal pH for this cations adsorption should be 5 or 6 [33].

3.3 Surfactant Dosage

The water contaminant removal rate of surfactant-modified clay adsorbents is strongly affected by the amounts of surfactant added to the clay materials. Previous research efforts have shown that increased amounts of cationic surfactants have led to an elevation in adsorption capacity due to the increased amount of surfactant entering the clay layers, which enlarges the interlayer space. Therefore, this can enhance the organophilic ability and hydrophobicity and thus, the adsorption capacity enhancement [7].

4 Adsorption Mechanisms

4.1 Organic Pollutants Removal

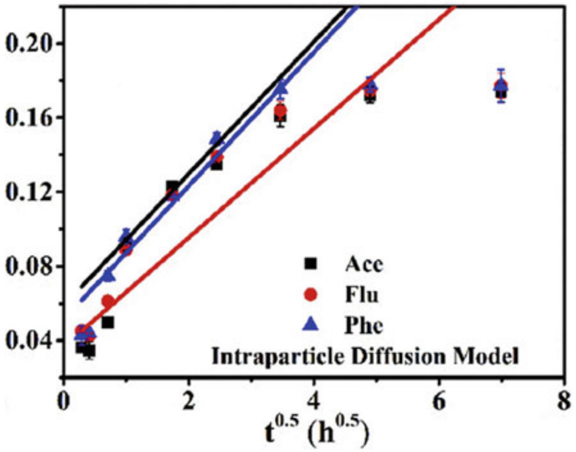
The adsorption mechanism towards pollutants in water with surfactant-based organoclays is based on the structural and surface properties of both natural clay and functional groups of the surfactant. During these mechanisms, electrostatic interaction, ion exchange, surface complexation, surface hydrophobicity, and hydrogen bonding are mainly involved [18, 32]. The absorption mechanism of organic compounds such as polycyclic aromatic hydrocarbons (PAHs) is fundamentally influenced by the hydrophobicity of the surfactant-modified clay adsorbents and the molecular structure and the weight of PAHs, based on π–π stacking. The adsorption mechanisms which lead to high PAH accumulation have been related to the ability of benzene rings in PAH contaminants to the formation of π–π complexes between the active site on surfactants and π-electrons of benzene rings. In addition, a previous study has suggested that the hydrophobic interactions between adsorbent surfaces and PAH compounds can be generated due to the intermolecular interactions (i.e., Van der Waal forces) [10].

In studying adsorption processes, adsorption kinetics is considered the most significant step and it describes the relationship between the contact time and the amount of contaminant adsorbed. The adsorption kinetic models such as PSO, PFO, intraparticle diffusion, and Elovich are commonly applied in adsorption process investigation for PAH removal by surfactant-modified clay adsorbents. A kinetic study that used cetyltrimethylammonium bromide (CTAB) modified montmorillonite has indicated the involvement of pore mass transfer and the significant role of chemical adsorption in the PAHs adsorption process. It has further described that, at the initial stage of the adsorption, external mass transfer resistance can be overcome by the concentration gradient which constitutes a high adsorption force. Moreover, this has led to the easy capture of PAHs due to the increased affinity of the active sites on the modified clay adsorbent. As the lower affinity active sites get filled, the adsorption rate change from fast to slow and at last, reach equilibrium. During the mass transfer process, the contaminant is adsorbed across the boundary layer around the clay adsorbent by the external mass transfer adsorbing on modified clay active sites through chemical and physical bonds. The contaminants (adsorbate) enter the interior of the clay adsorbent through the internal mass transfer (pore wall or holes). The intraparticle diffusion model is generally used to investigate the control mechanism of the contaminant adsorption process. In the previously mentioned study, the linear form of the intraparticle diffusion model (Fig. 1) equation ($Q_t = K_i t^{0:5} + C$ where K_i (min^{-1}) is the diffusion rate parameter of the intraparticle diffusion model) had been applied. The higher slope of the curve at the beginning indicates the rapid adsorption occurring on the modified clay surface and with time the adsorption rate gets slowed down until reaches the equilibrium. During the adsorption process, particle diffusion and the boundary layer diffusion which are the slowest steps control the rate of the entire process [7].

4.2 Inorganic Pollutants Removal

According to some reported literature, electrostatic interaction plays a major role in anionic pollutant adsorption mechanisms by surfactant-modified clay materials. In a study that tried to remove PO_4^{3-} by LaO-modified Montmorillonite (LaOMt) and Gemini surfactant-modified Montmorillonite (Mt) clay, it has been suggested that the availability of 2p orbitals has the ability to lead to successful adsorption by LaOMt. Further, this electrostatic interaction is reported as favorable at high pH values. Further in this study, because certain phosphate adsorption sites were imbedded and eventually became accessible as a result of the hydration of LaOMt in solutions, Elovich model fitting has revealed that phosphate absorption was a diffusion-limited process. Moreover, the good fitting of nitrate uptake by the pseudo-second-order model indicated that the chemisorption dominated the adsorption process which

Fig. 1 Intraparticle diffusion for the PAH (Ace–acenaphthene, Flu–fluorene, and Phe–phenanthrene) adsorption onto surfactant (CTAB) modified montmorillonite clay [7]



might involve the valency forces through sharing or exchanging electrons between adsorbate and adsorbent [16].

An arsenic adsorption study by the surfactant (HDTMA) modified smectite has suggested an anion exchange mechanism during the adsorption process as follows [20].

$$\begin{aligned}&[\mathrm{HDTMA-smectite}]\,\mathrm{Br^-(s)} + \mathrm{H_2AsO_4^-(aq)}\\&\quad\rightarrow [\mathrm{HDTMA-smectite}]\,\mathrm{H_2AsO_4(s)} + \mathrm{Br^-(aq)}\end{aligned} \tag{1}$$

$$\begin{aligned}&[\mathrm{HDTMA-smectite}]\,\mathrm{Br^-(s)} + \mathrm{HAsO_4^{2-}(aq)}\\&\quad\rightarrow [\mathrm{HDTMA-smectite}]\,\mathrm{HAsO_4(s)} + \mathrm{2Br^-(aq)}\end{aligned} \tag{2}$$

Counter ion available in HDTMA surfactant and Br- is exchanged with $HAsO_4{}^{2-}$ ions. Smectite consists of Si–OH bonds at the outer surface which undergoes protonate or deprotonate depending on the solution pH. Therefore, higher arsenic adsorption can be observed at low pH. pH above 8, the surface becomes negatively charged then repulsion occurs [20]. In another study arsenic ion adsorb into HDTMA-Br modified kaolin clay has been described via chemisorption (As(V)) and physisorption (As(III)). The external surface adsorption onto the micropore surface attaches As(III) physically. Due to the intraparticle diffusion into the micropore and mesopore of the adsorbent arsenic adsorption can undergo ion exchange with OH- as well [19].

In addition to the above, metal ion adsorption mainly occurs through chemical complexation [17]. As potential adsorption mechanisms of Cd^{2+} by magnetic bentonite clay (BS-MBt) modified with surfactants, ion exchange, surface complexation, and electrostatic interaction have been proposed. In addition, chelation has also considered as a Cd^{2+} adsorption mechanism onto BS-MBt. It has been reported that, the presence of amidocyanogen group in BS-CT-MBt has an inhibitory effect on the

Cd^{2+} adsorption owing to electrostatic repulsion. In contrast, electrostatic attraction functions to induce the Cd^{2+} adsorption on BS-SDS-MBt due to the presence of sulfur group in the material.

Furthermore, an interesting phenomenon has been reported for the Cd^{2+} adsorption on surfactant modified clay minerals based on their negative and positive charges. A slight difference in the Cd^{2+} adsorption capacity under acidic pH (3.0) condition has been observed between the positively charged BS-MBt and the negatively charged BS-MBt. Comparatively the positively charged BS-MBt has a slightly high adsorption capacity. This phenomenon has been attributed to the interactions between organoclays and metal ions through ion exchange but surface complexation has a great contribution than electrostatic interactions. Due to more exposed negatively charged functional groups (such as carboxyl and sulfo groups), BS-SDS-MBt had more negative charges than MBt. This has the ability to further increase the Cd^{2+} adsorption capacity of BS-MBt and BS-SDS-MBt. However, BS-CT-MBt has shown poor Cd^{2+} adsorption for Cd^{2+} among adsorbents and has demonstrated a poorer Cd^{2+} adsorption ability than MBt. On the other hand, BS-CT-MBt was positively charged over the whole pH range, which had a repellent electrostatic effect on Cd^{2+} and resulted in a noticeable decrease in Cd^{2+} adsorption onto BS-CT-MBt [30] (see Figs. 2 and 3).

The major thermodynamic parameters such as enthalpy, entropy, and Gibbs free energy are examined to analyze the scientific application of a process. The values

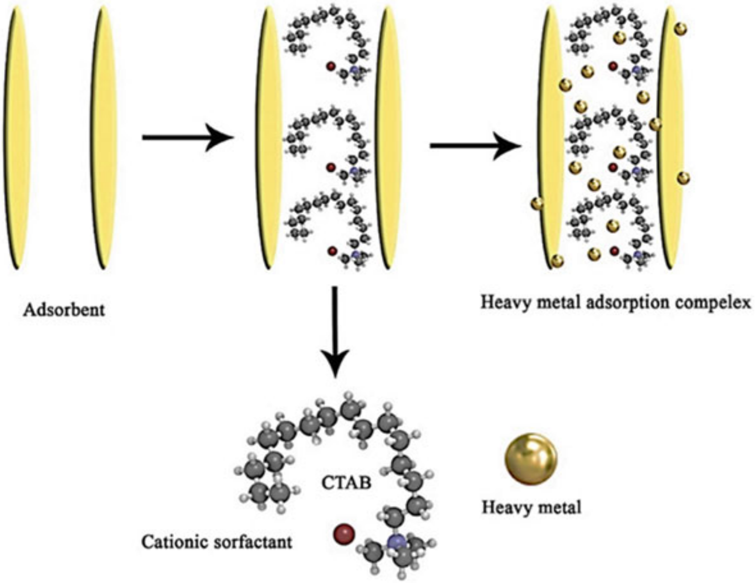


Fig. 2 A schematic of the adsorption process of heavy metals using adsorbents modified by cationic surfactants [32]

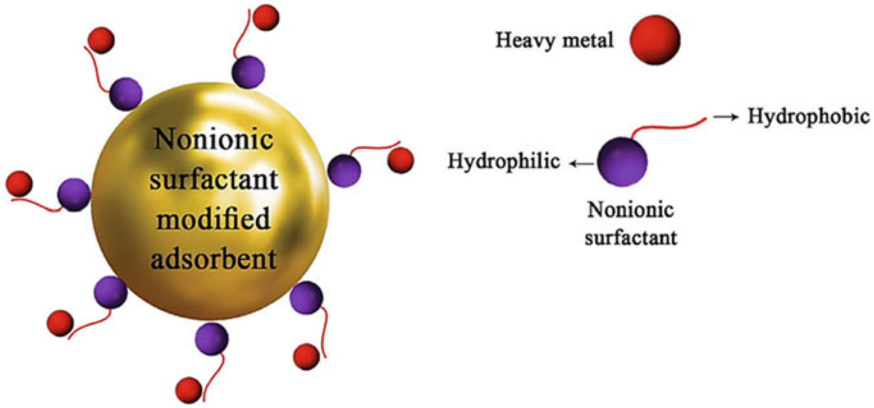


Fig. 3 A schematic of the uptake process of heavy metals using adsorbents modified by non-ionic surfactants [32]

of ΔH∘ and ΔG∘ are negative for almost all modified clay adsorbents, showing that the inorganic pollutant adsorption process is exothermic and spontaneous.

5 Summary

The adsorption technique is a better-suited water pollutant remediation approach among other approaches. Further, surfactant modification of clay minerals outlined here has the potential to remove organic and inorganic water contaminants more effectively. Surfactant types including cationic, anionic, non-ionic, and zwitterionic have been applied in modifying different clay minerals for pollutant adsorption while undergoing several adsorption mechanisms. Moreover, the adsorption performance is strongly affected by the factors such as type and size of the surfactant, surfactant dosage, adsorbent dosage, pH value of the adsorption media. In conclusion, in order to fulfill the fundamental requirements of good-quality water, surfactant-modified clay adsorbents can be considered excellent materials.

References

1. Abdel Ghafar, H.H., et al.: Removal of hazardous contaminants from water by natural and Zwitterionic surfactant-modified clay. ACS Omega **5**(12), 6834–6845 (2020). https://pubs.acs.org/doi/10.1021/acsomega.0c00166
2. Ahmad, N., et al.: Visible light-conducting polymer nanocomposites as efficient photocatalysts for the treatment of organic pollutants in wastewater. J. Environ. Manag. **295**(June), 113362 (2021). https://doi.org/10.1016/j.jenvman.2021.113362

3. Almasoud, N., et at.: A solid phase extraction based UPLC-ESI-MS/MS method using surfactant-modified clay as extraction sorbent for the removal and determination of rhodamine B in industrial wastewater samples. Desalin. Water Treat. **195**, 222–231 (2020). https://doi.org/10.5004/dwt.2020.25896
4. Barakan, S., Aghazadeh, V.: The advantages of clay mineral modification methods for enhancing adsorption efficiency in wastewater treatment: a review. Environ. Sci. Pollut. Res. (Atia 2005) (2020)
5. Belachew, N., Hinsene, H.: Preparation of cationic surfactant-modified kaolin for enhanced adsorption of hexavalent chromium from aqueous solution. Appl. Water Sci., 1–8 (2020). https://doi.org/10.1007/s13201-019-1121-7
6. Choi, N., et al.: Adsorption behaviors of modified clays prepared with structurally different surfactants for anionic dyes removal **28**(2), 0–3 (2023)
7. Dai, W.J., et al.: Adsorption of polycyclic aromatic hydrocarbons from aqueous solution by organic montmorillonite sodium alginate nanocomposites. Chemosphere **251**, 126074 (2020). https://doi.org/10.1016/j.chemosphere.2020.126074
8. Deng, L., et al.: Dynamic benzene adsorption performance of microporous TMA+-exchanged montmorillonite: the role of TMA+ cations. Microporous Mesoporous Mater. **296**(December 2019) (2020). https://doi.org/10.1016/j.micromeso.2019.109994
9. Hedayati, M.S., et al.: Removal of polycyclic aromatic hydrocarbons from aqueous media using modified clinoptilolite. J. Environ. Manag. **273**(March), 111113 (2020). https://doi.org/10.1016/j.jenvman.2020.111113
10. Hedayati, M.S., Abida, O., Li, L.Y.: Adsorption of polycyclic aromatic hydrocarbons by surfactant-modified clinoptilolites for landfill leachate treatment. Waste Manag. **131**(November 2020), 503–512 (2021)https://doi.org/10.1016/j.wasman.2021.06.033
11. Jiang, J.Q., Ashekuzzaman, S.M.: Development of novel inorganic adsorbent for water treatment. Curr. Opin. Chem. Eng. **1**(2), 191–199 (2012).https://doi.org/10.1016/j.coche.2012.03.008
12. Kausar, A., et al.: Dyes adsorption using clay and modified clay: a review. J. Mol. Liq. **256**, 395–407 (2018). https://doi.org/10.1016/j.molliq.2018.02.034
13. Krishna, B.S., et al.: Surfactant-modified clay as adsorbent for chromate. Appl. Clay Sci. **20**(1–2), 65–71 (2001). https://doi.org/10.1016/s0169-1317(01)00039-4
14. Lazaratou, C.V., Vayenas, D.V., Papoulis, D.: The role of clays, clay minerals and clay-based materials for nitrate removal from water systems: a review. Appl. Clay Sci. **185**(June), 105377 (2020). https://doi.org/10.1016/j.clay.2019.105377
15. Lin, S., Juang, R.: 1-s2.0-S0304389402000262-main, vol. 92, pp. 315–326 (2002)
16. Luo, W., et al.: Journal of Water Process Engineering Lanthanum/Gemini surfactant-modi fi ed montmorillonite for simultaneous removal of phosphate and nitrate from aqueous solution. J. Water Process Eng. **33**(July 2019), 101036 (2020). https://doi.org/10.1016/j.jwpe.2019.101036
17. Malakul, P., Srinivasan, K.R., Wang, H.Y.: Metal adsorption and desorption characteristics of surfactant-modified clay complexes. Ind. Eng. Chem. Res. **37**(11), 4296–4301 (1998). https://doi.org/10.1021/ie980057i
18. Mao, S., Gao, M.: Functional organoclays for removal of heavy metal ions from water: a review. J. Mol. Liq. **334**, 116143 (2021). https://doi.org/10.1016/j.molliq.2021.116143
19. Mudzielwana, R., Gitari, M.W., Ndungu, P.: Performance evaluation of surfactant modified kaolin clay in As(III) and As(V) adsorption from groundwater: adsorption kinetics, isotherms and thermodynamics. Heliyon **5**(11), e02756 (2019). https://doi.org/10.1016/j.heliyon.2019.e02756
20. Mukhopadhyay, R., et al.: Comparison of properties and aquatic arsenic removal potentials of organically modified smectite adsorbents. J. Hazard. Mater. **377**, 124–131 (2019). https://doi.org/10.1016/j.jhazmat.2019.05.053
21. Mundkur, N., et al.: Environmental Nanotechnology, Monitoring & Management Synthesis and characterization of clay-based adsorbents modified with alginate, surfactants, and nanoparticles for methylene blue removal. Environ. Nanotechnol. Monitor. Manag. **17**(September 2021), 100644 (2022). https://doi.org/10.1016/j.enmm.2022.100644

22. Munir, M., et al.: Effective adsorptive removal of methylene blue from water by didodecyldimethylammonium bromide-modified brown clay. ACS Omega **5**(27), 16711–16721 (2020). https://pubs.acs.org/doi/10.1021/acsomega.0c01613
23. Mustapha, S., et al.: Application of TiO_2 and ZnO nanoparticles immobilized on clay in wastewater treatment: a review. Appl. Water Sci. (2020)https://doi.org/10.1007/s13201-019-1138-y
24. Najafi, H., et al.: A comprehensive study on modified-pillared clays as an adsorbent in wastewater treatment processes. Process Saf. Environ. Prot. **147**, 8–36 (2021). https://doi.org/10.1016/j.psep.2020.09.028
25. Nasrollahpour, S., et al.: Application of organically modified clay in removing BTEX from produced water. In: Geo-Congress 2020 GSP, vol. 319, pp. 275–283 (2020)
26. Nassar, M.Y., et al.: Adsorptive removal of manganese ions from polluted aqueous media by glauconite clay—Functionalized chitosan nanocomposites. J. Inorg. Organomet. Polym. Mater. (Ii) (2021). https://doi.org/10.1007/s10904-021-02028-8
27. Onwuka, K., et al.: Hexadecyltrimethyl ammonium (HDTMA) and trimethylphenyl ammonium (TMPA) cations intercalation of Nigerian bentonite clay for multi-component adsorption of benzene, toluene, ethylbenzene and xylene (BTEX) from aqueous solution: equilibrium and kinetic stud. J. Anal. Tech. Res. **02**(02), 70–95 (2020). https://doi.org/10.26502/jatri.013
28. Oussalah, A., Boukerroui, A.: Removal of cationic dye using alginate–organobentonite composite beads. Euro-Mediterr. J. Environ. Integr. **3**, 1–10 (2020). https://doi.org/10.1007/s41207-020-00199-3
29. Rahmani, S., et al.: Removal of cationic methylene blue dye using magnetic and anionic-cationic modified montmorillonite: kinetic isotherm and thermodynamic studies. Appl. Clay Sci. **184**(July 2019), 105391 (2020). https://doi.org/10.1016/j.clay.2019.105391
30. Ren, S., et al.: Comparison of Cd^{2+} adsorption onto amphoteric, amphoteric-cationic and amphoteric-anionic modified magnetic bentonites. ECSN, p. 124840 (2019). https://doi.org/10.1016/j.chemosphere.2019.124840
31. Satouh, S., et al.: Adsorption of polycyclic aromatic hydrocarbons by natural, synthetic and modified clays. Environ.—MDPI **8**(11) (2021). https://www.mdpi.com/2076-3298/8/11/124
32. Tamjidi, S., et al.: Improving the surface properties of adsorbents by surfactants and their role in the removal of toxic metals from wastewater: a review study. Process Saf. Environ. Prot. **148**, 775–795 (2021). https://doi.org/10.1016/j.psep.2021.02.003
33. Tohdee, K., Kaewsichan, L., Asadullah: Enhancement of adsorption efficiency of heavy metal Cu(II) and Zn(II) onto cationic surfactant modified bentonite. J. Environ. Chem. Eng. **6**(2), 2821–2828 (2018). https://doi.org/10.1016/j.jece.2018.04.030
34. Wang, H., et al.: Colloids and Surfaces A: Physicochemical and Engineering Aspects Cationic surfactant modified attapulgite for removal of phenol from wastewater. Colloids Surf. A Physicochem. Eng. Aspects **641**(February), 128479 (2022). https://doi.org/10.1016/j.colsurfa.2022.128479
35. Wasewar, K.L., et al.: Process intensification of treatment of inorganic water pollutants. In: Inorganic Pollutants in Water. INC (2020). https://doi.org/10.1016/B978-0-12-818965-8.00013-5
36. Xiao, T., et al.: Colloids and Surfaces A: Physicochemical and Engineering Aspects Adsorption of tungstate using cationic Gemini surfactant-modified montmorillonite: influence of alkyl chain length. Colloids Surf. A Physicochem. Eng. Aspects. **629**(September), p. 127484 (2021). https://doi.org/10.1016/j.colsurfa.2021.127484
37. Zhang, T., et al.: Removal of heavy metals and dyes by clay-based adsorbents: from natural clays to 1D and 2D nano-. Chem. Eng. J., 127574 (2020). https://doi.org/10.1016/j.cej.2020.127574

Clay Polymer Composites

Imaging Methods for Characterization of Polymer Clay Composites

R. T. Mohotti, C. V. Ihalavithana, and N. M. Adassooriya

Abstract Clays and composites have received quite a deal of attention recently mostly due to its advanced properties while being environmentally and economically feasible. Polymer clay composites are made up of synthetic or natural clay combined with a polymer. While each constituent has its own advantages when incorporated together, various properties of interest can be improved by numerous methods such as varying the aspect ratio, mechanical and physical dimensions, and the intercalation properties. In order to establish an optimal relationship between the structure and its properties, proper methods are needed to characterize these morphologies. Up to date, various methods such as optical, electron and magnetic imaging techniques, light scattering, and microscopic imaging in 2D and 3D have been used. Each method is used based on the required sensitivity and output. This chapter focuses on the imaging techniques of characterization of clay polymer composites.

1 Introduction

Over the years, it has been seen that the development of polymer clay composites has been on the rise, owing to the wide array of properties of interest that the composite product brings. The incorporation of even a relatively small amount of clay in a polymer matrix has been seen to increase the mechanical and material properties of the polymer vastly in comparison to the polymer or the filler material alone. Properties such as mechanical, thermal, electric barriers, electrical conductivity, water absorption are improved and enhanced with composite formation. The interfacial interactions of the polymer and the clay filler can be viewed as the reason for these enhanced properties. The preparation of polymer clay composites can also be applied commercially and is thereby gaining a huge revenue. As of today, a significant amount

---

R. T. Mohotti · C. V. Ihalavithana · N. M. Adassooriya (✉)
Department of Chemical and Process Engineering, University of Peradeniya, Peradeniya, Sri Lanka
e-mail: nadeeshm@eng.pdn.ac.lk

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_12

of research has been done with respect to synthesis methods, applications, materials, and properties. However, we are yet to discover the mechanisms of the enhancement of these materials.

Clay is made up of silicates stacked on top of each other bound together by Van der Waals forces. They are generally anisotropic [1], hydrophilic in nature, and incompatible with most polymers. To make these combinations more compatible, surface modification, and functionalization of clay can be done which disperses the clay in the polymer matrix [2]. The applications of clay can be attributed to its structure and composition, and properties such as particle size, surface chemistry, shape, surface area, viscosity, color, plasticity, absorption, adsorption, and much more.

Polymers are made up of large molecules where molecules are linked to each other through covalent bonds. They can be amorphous or semi-crystalline in structure. Properties of polymers can be tuned through the incorporation of clay fillers. Polymer clay composites are formed by separating the individual silicate layers of the clay in the polymer. This helps in more effective functionality of the individual clay layers. Then, by a small incorporation of clays in the polymer, the material properties like modulus, gas barrier properties, heat distortion temperature, etc. can change vastly.

Based on the interphase forces between the polymer and the clay, there are various morphologies [3], namely intercalated composites, flocculated composites, and exfoliated composites. Intercalated composites are those where alternative layers of clay and polymer chains are inserted, and the structure is crystallographically regular. With a structure similar to intercalated composites, flocculated composites are formed, however, due to the interaction of the edges of the hydroxyl groups of the silicate, flocculation occurs. Exfoliated composites are those where individual clay layers are randomly separated in the polymer matrix. The separation distance depends on the clay loading. These behavioral changes can be observed through imaging techniques, and conclusions can be reached as to whether synthesis has been performed properly.

In order to understand the behavior of the composites with the variations of the polymer-filler interface, morphology, and nature, it is helpful to dive deeper into the structure of the composites and visualize the 2D and 3D structures.

1.1 Characteristics of Interest of Clay Composites

Many of the improved properties of polymer clay composites arise from the extensive interface and interactions between the polymer and the clay. Thus, the intercalation, exfoliation, and clay polymer interactions with respect to the composition of the components and processing conditions are crucial to be identified in order to better understand the relationships of property escalation. The higher the clay dispersion and exfoliation, the better the properties. Interactions at interfaces, confinement of polymer chains at clay interlayer galleries can affect thermodynamic and kinetic processes responsible for dynamic behavior.

Many important chemical and physical properties are governed by surfaces and the boundaries of the grains in the material. Surface analysis can be performed for an extensive representation of these properties.

Volatiles in the composite are released during degradation. Delaying the volatile matter release can delay the degradation of the composite, and this knowledge on the degradation characteristics of the composite can be useful in various applications. The degree of exfoliation, distance between clays and volume fraction can all affect the degradation behavior [4].

The properties of a clay polymer composite are a function of filler size, shape, dispersion, and interactions of the matrix and the filler. Information on the composite's morphology, conductivity, fracture points, etc. can be identified.

1.2 Available Imaging Techniques

Typically, various imaging and characterization techniques are used in combination for a better comprehension of the relationships of clay polymer interactions.

The current imaging techniques available in characterization can be categorized as optical, magnetic, X-Ray, electron microscopic imaging. Though a plethora of techniques can be identified in the current context, this chapter will be focusing on a few main techniques that are abundantly used in the characterization of polymer clay composites. To obtain a better understanding of the results, it is advised to crosscheck the results with other characterization techniques. Hence, this chapter will also outline a few main other techniques that would be useful in getting a precise analysis of the results.

- Optical imaging:
  - Fluorescence Spectroscopy
  - Laser Scanning Confocal Microscopy (LSCM)
- Magnetic imaging:
  - Nuclear Magnetic Resonance imaging (NMR)
- Electron microscopy:
  - Scanning Electron Microscopy (SEM)
  - Transmission Electron Microscopy (TEM)
- Probing techniques:
  - Atomic Force Microscopy (AFM)
- X-Ray techniques:
  - X-Ray tomography

- Other characterization techniques of interest:
  - X-Ray Diffraction (XRD)
  - Infra-Red techniques (IR)
  - Raman Spectroscopy

The chapter focuses on a brief introduction to the working of the equipment, and the applications of it. Furthermore, the sample preparation and analysis of results will be highlighted briefly with its applications in an environmental approach with an overlay of its advantages, disadvantages, and further modifications. The reader is directed to further reading in terms of the principles and operation of the technique and equipment. Finally, choosing the right technique for the relevant application is essential, since this determines the accuracy and the interpretation of the output, and therefore this factor will be highlighted in this chapter as well.

2 Imaging Techniques

2.1 Electron Microscopy

Over the past years, electron microscopy (EM) has been a technique of high demand due to the versatile and the high-resolution imaging performance it possesses. EM uses focused accelerated electrons as the source and thus has a wavelength that is about 1000 times smaller than that of visible light, making it useful for imaging. Images are created by electrons falling on the surface, and higher energy electrons have the ability of penetration, creating under the surface images. However, limitations to this technique do exist, such as, the need of a vacuum for the emission and transmission of electrons and the damage caused to samples by electron beams. Despite this, a variety of electron microscopy techniques do exist, their applications extending to numerous fields of study. This chapter will focus on two of the main techniques used abundantly, the Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM).

2.1.1 Scanning Electron Microscopy (SEM)

The scanning electron microscope or SEM is an ideal choice for the imaging of the surface morphologies of a clay composite due to its easy sample preparation, user friendly interface, and simple interpretation of results. The SEM offers 3-dimensional images of high resolution and can be used for characterizing various other properties of interest as well.

The SEM operates on a simple principle of detecting secondary backscattered electrons. An electrical optical column having an electromagnetic lens demagnifies an electron beam so that it can be directed to the surface. Atomic sized electrons through the beam with energies in the range of 1–50 keV are then scanned across the specimen surface. The resulting signal is collected by an electron beam detector. The resolution of the final image obtained depends on the electron beam spot. This is inversely proportionate to the accelerating voltage. Accelerating voltage is the voltage given to accelerate the electrons from the electron gun and provide an image. This determines the speed of the electrons, and the resolution of the image.

The scanning electron microscope provides in-depth details of various properties of interest in the area of clay composites. The main applications of the SEM are in obtaining surface morphology, composition of materials, particle arrangement, particle boundary relationship, growth mechanics of the crystals and topography (roughness, texture).

One main point of concern of the SEM is its sample preparation technique. Based on the working principle of the SEM, the electrons have to pass through the surface of the sample, and scatter/reflect back to the electron detector. For a better accuracy of the results, it is important that the sample remains unaltered. The electrons that impinge from the beam should dissipate through the specimen and to the stage without accumulation for a better image to be shown, and a conductive path should be formed for this purpose. Thus, the sample preparation will differ for metals and non-metals based on the conductivity of the material.

For polymer clay composites, the material preparation involves the following steps. In metallic compounds, no additional preparation is required, except for cleaning and mounting on the specimen holder. Nonconductive specimens need to be coated with a conductive material since they tend to charge and accumulate electrons on the surface. They are usually coated with a thin electrically conductive material like carbon or gold through means of sputter coating or thermal evaporative coating.

The SEM detects secondary electrons and backscattered electrons. If the incident electron beam falls on a cavity or a flat surface, the image results in a dark region. A bright area is seen if the primary beam impinges on an asperity since a higher number of electrons would then leave the surface.

Interpretation of an SEM image is simple, and the point of analysis varies based on the objectives of the research. Various research were highlighted in relevance to soil sciences which used SEM imaging to identify surface characteristics. Cavallaro [5] prepared nanocomposites of polyethylene glycol filled with clay nanotubes (HNT). The amounts of HNT varying the properties were studied. SEM was used to observe the filler dispersion in the polymer matrix, and the results showed filler dispersion in the core, surface, and micro edges of the material. The sizes of craters in the surface were also analyzed.

Notable research in the area of nitrogen inhibition was conducted by Saurabh where nanoclay polymer composites were synthesized with bentonite and acrylic acid and loaded with urea and nitrification inhibitors. SEM images have revealed pores and cracks, indicating the roughness of the surface. The homogenous nature of the dispersion of the clay in the polymer was also observed [6].

Clay polymer composites are used as controlled release fertilizer and the surface morphology is an important point of concern since it relates to information on release rates, absorption, etc. Mandal [7] observed the fractured morphology of a composite that was sputter coated with gold-palladium for SEM observation and observed increased roughness that showed variations in surface texture. Clay aggregates were scattered non-homogeneously that indicated exfoliated nature which could be devised to determine moisture characteristics, release patterns, and biodegradability. Similar research [8] in preparing nanocomposites for rainfed agriculture also used SEM to identify the sizes of particles as to whether they are nano-sized. The texture was also observed for better characterization and conclusion on release patterns.

SEM is beneficial in terms of its versatile uses, 3-dimensional imaging, and easy operation. However, this is a costly and large equipment and has to be housed such that it has no magnetic, electric, or vibrational interference.

2.1.2 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) with a number of imaging modes, is now a highly sought method for particle size analysis and size distribution of particles from less than a few nanometers up to micrometers [9].

The Transmission Electron Microscope features the formation of images of atomic arrangements of materials. It provides a microstructural view with the interfaces and material structures.

The principle of operation of the TEM is that a high energy beam of electrons is accelerated through a very thin sample of the specimen, and the interaction that occurs between the electrons and atoms is used to highlight certain features of interest. A beam is focused on the specimen and part of it is transmitted back depending on the thickness and electron transparency of the specimen. It is the principle of the optical microscope but instead of light uses electrons, providing a better resolution, and hence, very detailed images of microstructures.

An aperture is placed in the back focal plane to select only the transmitted beam for image formation. Scattered and diffracted beams are not taken into consideration, with the resulting image consisting of these areas where fewer electrons transmit are darker, and those that do not scatter or more electrons transmit appear lighter. Furthermore, the intensity of the transmitted beam depends on absorption, and hence the thicker zones or those that are heavier would result in darker zones in the image, while the rest will appear lighter [10].

TEM is useful in characterizing the 3D microstructure: outlining the dimensions, orientation, distribution, morphology, surface area, etc. Quantizing these details will better portray the thermal behavior of the composite, thus giving specific information about the characteristics of the final composite. TEM also provides information on the spatial distribution and structural homogeneities.

In all TEM sampling, the sample preparation is a key step that determines the final results of the analysis. Sample preparation is a bit rigorous when analyzing a sample through the TEM. Ultrathin slices of the sample need to be obtained since transmission with minimal energy loss has to occur, and this can be done by extracting sections using a ion focused beam. Thin polymer films can also be manufactured by deposition of material to a thin layer depending on the material. The accelerating voltage usually used for TEM is 100 keV for a better resolution [9].

Special considerations should be extended to exposure times and exposure voltage with layered silicates [11]. Exposure time cannot be very large, then clay layers can disappear from the image and interlayer spacing changes. This occurs since under electron beams the clay sample can dehydrate and collapse with prolonged times.

Once the clay is integrated in the polymer matrix, the extent of clay platelet separation determines the microstructure of the composite, and hence the final properties of the composite [4]. To investigate this phenomenon, TEM is useful here in terms of providing a direct observation of the degree of exfoliation in the matrix [4]. However, TEM only provides a 3D projection of the orientation and dimension of the objects on a 2D plane, which cannot be accurately measured [4]. Therefore, the characterization becomes qualitative and indecisive. Individually characterizing each layer is possible to minimize this disadvantage, however, this is time consuming and impractical.

Sarkar et al. synthesized a polymer composite with soil clay suitable as a superabsorbent for water and nutrient uptake [12]. This was analyzed using the TEM. The sizes of the particles were critical in identifying whether nanoparticles were formed for a better absorbency. Using the sizes of the TEM images and an aspect ratio, dimensions can be obtained. This value was cross checked with that obtained from the XRD results. Disparities that occurred were related to the bonding nature of the components.

A clay polymer composite was prepared as a biodegradable packaging material [13]. Characterization was conducted by TEM with an accelerating voltage of 100 kV. Ultrathin slices (~50 nm) were cut using a diamond knife. By observing the TEM images, a representation of the agglomeration together with the intercalation zones was observed.

2.2 Probing Techniques

2.2.1 Atomic Force Microscopy (AFM)

Atomic force microscopy or AFM is ideally suited for characterizing nanoparticles and nanocomposites. It provides information on a variety of physical characteristics, such as size, morphology, surface texture, and roughness, in both qualitative and quantitative forms. It is also possible to determine statistical information such as size, surface area, and volume distributions [14].

Unlike the electron microscope, AFM provides a three-dimensional profile and can be conducted in ambient air without any special treatment (such as metal-carbon coating) that would change or damage the sample [15].

AFM is performed by using a probe, which includes a tip fixed to the free end of a flexible cantilever. The probe scans the sample, and tip moves in response to tip-surface interactions. This induces a change in cantilever deflection that is recorded by means of different techniques, mainly using the optical lever system. The processing signals generated by these interactions allow for analyzing local properties of the object [15, 16].

The two principal operating modes of AFM are contact and tapping. In contact mode, the AFM tip is continuously in contact with the surface. Tapping is the most used mode for imaging. In the tapping mode, the cantilever is vibrated above the sample surface reducing shear force associated with tip movement as the tip is in contact with the surface only intermittently [15].

AFM analysis is one of the most helpful analytical tools for clay composites in environmental applications. Three-dimensional (3D) AFM images were obtained for both polysulfone (PSf) and organoclay embedded PSf nanocomposite membranes prepared for arsenate removal from contaminated surface water. Since contact mode may finally damage the membrane, surface tapping mode was used. The images revealed that the nanocomposite membranes presented larger roughness parameter than neat PSf membrane on account of the increased pore size on membrane surface [17].

Foroutan and his team used AFM to assess the surface properties and to evaluate the surface roughness of Iranian natural clay and clay/Fe–Mn composite to remove toxic arsenic from the liquid environment. The results showed an increase in roughness on the surface of the clay/Fe–Mn composite due to the presence of Fe–Mn which could lead to a higher specific surface area, and thus, a higher number of sites for the adsorption of contaminants [18].

The AFM images of sodium alginate–halloysite clay composite aerogel (SAHA) for oil/water separation prepared via a two-step synthesis procedure, including ionic crosslinking and freeze-drying were compared with sodium alginate aerogel (SA) to quantify the surface roughness. From the amplitude trace scan and 3D images, the SAHA aerogel showed an increase in surface roughness having unsmooth and uneven surfaces with major crest and trough features [19].

Matusik and his team used AFM to confirm a very good dispersion of kaolinite nanotubes which undoubtedly had a significant impact on the measured mechanical parameters and high homogeneity of biodegradable polylactide/clay composite obtained by an intercalation/deintercalation method as an environmentally conscious alternative [20].

2.3 Magnetic Imaging Techniques

2.3.1 Nuclear Magnetic Resonance (NMR) Spectroscopy and Imaging

NMR Utilizes the magnetic resonance of the nucleus to determine the structure of compounds. Over the past years, NMR has grown to be a useful tool in determining the physical and chemical properties of compounds, featuring molecular identity and structure. When polymers are intercalated amidst clay molecules, it gives rise to molecular reordering that changes chain conformation and mobility. Based on the specific application, NMR is a versatile tool that offers a plethora of applications in determining these changes. Properties of clay composites can be studied as a function of surfactant loading, nature of the head group and length of the hydrocarbon chain [21]. NMR is the only tool that provides angstrom resolution of molecules in solution and non-crystalline solids.

NMR is a technique that is based on the phenomena of external radiation interacting with atomic nuclei. In the midst of a magnetic field, NMR-active nuclei align themselves in two orientations parallel or antiparallel to the magnetic field. This is, however, hard to detect in an NMR experiment since the magnetic field is too strong in that direction. It is helpful if the magnetization of the z component is transferred to the *x*–*y* plane. Magnetic resonance is achieved when external irradiation occurs, where orientations of the nuclei are changed due to transitions between energy levels. Therefore, a magnetic pulse is applied perpendicular to the z direction that reaches the resonance of the nuclear spins and transfers a vector component to the *x*–*y* plane. Then a relaxation process occurs where the nuclei lose its energy which produces a signal detected by the detector. Through a Fourier transformation, this signal is plotted as a peak. The separation of energy levels depends on not only the nucleus and its magnetic spin, but also the environment of the nucleus. This is called chemical shielding and can be used to distinguish molecules separately. The effect of shielding results in fine structuring of peaks. Imaging is achieved through the application of a linear magnetic field gradient on top of the initially applied magnetic field. The gradient can be rotated electronically and a series of projections at different angles are obtained to create an image [22].

As mentioned, NMR is a versatile tool for obtaining information on the molecules of a sample. Chemical groups and structure of the molecule can be identified, giving information on the content and purity of the molecules, extending these to getting information on phase changes, solubility, diffusion, etc. NMR can be used to complement FTIR data and provide additional information on intercalation of compounds. NMR studies have shown that presence of clay affects phase behavior and mobility depending on the composition, degree of exfoliation, synthesis and processing conditions.

Sample preparation does not require extensive steps, the sample size and solvent amount required depends on the type of the NMR. A major advantage of NMR is the ability to analyze samples without modification, and they do not need to be crystalline. The sample is dissolved in the NMR solvent, centrifuged, or directly packed in the sample holders. In analyzing specimens, focus has to be given to the main frequency, magnet strength and probe coil diameter and temperature [23].

A quantitatively study on the effects of the soil improvers on soil pore size distribution was done by Huang et al. Through characterization by NMR, they detected the soil pore structure effectively and non-destructively. Using the relaxation curve, the soil water characteristic curve was obtained [24].

A modified soil structure as a clay polymer composite was prepared [23]. An NMR imaging was conducted to observed adsorption and storage of free water by the resin.

Bouznik investigated the influence of surface treatment on water absorption in polymer composites using NMR spectroscopy and imaging techniques [25]. It was revealed that surface rough treatment improves water absorption, but this penetration of water occurs only through the surface in a thin layer [25]. The spatial water distribution was observed through imaging and preferable water pathways were seen. These results could be used for a variety of applications in many areas.

A study to mitigate the risk of soil erosion was conducted by introducing new clay polymer composites [26]. NMR was used to quantify the effects of the polymer and soil moisture absorption. The study revealed that the ratio and content of the polymer ADNB had an effect on the soil water characteristic curve and water holding capacity was improved.

2.4 Optical Imaging

2.4.1 Fluorescence Spectroscopy and Imaging

A direct visualization of the clays into the polymer of the composite materials are accomplished using fluorescence microscopy. The concepts underlying fluorescence and the optical separation it undergoes using filters do not change, but the design of microscopes changes to improve image contrast and spatial resolution. In this device, the entire specimen (or wide field of view) is concurrently illuminated by a parallel beam of light in order to excite the fluorophore(s) it contains via the filter block. Traditionally, the requisite wavelengths are chosen using specialized optical filters, and the excitation light is produced by a mercury or xenon high-pressure bulb (as described above). In contrast, just a small portion of the specimen is illuminated at a time using laser scanning microscopes, which requires the laser beam to scan across the specimen in order to produce a picture [27].

Commercial clays Cloisites Na^+, 30B, and 20A were utilized as fillers in polypropylene to create composites that could be examined using fluorescence microscopy. These clays were colored with the fluorescent dye Rhodamine B. Bright fluorescent images of Cloisite aggregates labeled with the dye were produced by fluorescence imaging, enabling non-invasive visualization of the 3D dispersion of the labeled fillers in the polymer matrix. To calculate the degree of dispersion, the images were examined for the size distribution of the fluorescence grains. According to the findings, Clo20A can spread uniformly throughout the polymer matrix to create a composite material [28].

Fluorescence spectroscopy refers to a type of spectroscopic method, where the fluorescence from the object of interest is measured after excitation with a beam of light (usually ultraviolet spectra) [29]. They are used to examine optical properties and electronic transition behaviors of hybrid composites such as clay polymer nanocomposites [30].

One of the widely used analytical tools in the determination of elemental/chemical composition of ceramic materials is the X-Ray fluorescence (XRF) spectroscopy. Following that, the behavior of Ghanaian-based bauxite red mud-Tetegbu clay composites were investigated for their applicability in the ceramic brick construction industry as a means of recycling bauxite waste. The XRF mineralogical composition of the samples were determined by XRF spectroscopy. For trace element analyses the sample was mixed with a PVA binder and pressed into a pellet using a 10-ton press [31].

Clay colloids and dialkyldimethylammonium surfactants combined in an aqueous suspension to form the composite films for catalysis application were studied by using fluorescence spectroscopy. The results concluded that the suspension method could be extended to composite films [32].

To address the restrictions shown by organic material such as being quenched after aggregation and low photo-thermal stability in the field of pollutant analysis, a novel mineral/dye composite material was prepared by intercalating a fluorescence molecule Rhodamine (R6G), into the interlayer space of montmorillonite (MMT). A fluorescence spectrophotometer with a photomultiplier tube and an excitation source with a xenon lamp was used to measure the photoluminescence excitation (PLE) and emission (PL) spectra. The emission spectrum indicating that too much or too little intercalation of R6G reduced the luminous intensity of R6G-MMT revealed a theoretical and experimental foundation for the development of novel supramolecular luminescent material [33].

A study to synthesize novel clay-biochar composites by incorporating montmorillonite (MMT) and red earth (RE) clay materials in a municipal solid waste biochar (MSW-BC) for the adsorptive removal of tetracycline (TC) from aqueous media used X-Ray Fluorescence (XRF) to do elemental analysis. The elemental compositions of the raw biochar and clay-biochar composites were presented and the percentage of Si and Al in MSW-MMT and MSW-RE clay-biochar composites did not increase with the clay modification of MSW-BC [34].

2.4.2 Confocal Laser Scanning Microscopy (CLSM)

One of the most significant developments in fluorescence imaging in recent years is confocal laser scanning microscopy (CLSM) and it belongs to the family of photonic imaging technologies. Although CLSM achieves much lower resolution than electron microscopy, it requires far less specimen preparation and is compatible with three-dimensional (3D) live imaging. *Confocal* refers to the process of just obtaining an image from the focal plane, with any noise brought on by sample thickness being optically eliminated. *Laser scanning* allows for point-by-point picture acquisition under localized laser stimulation as opposed to entire sample illumination as in traditional widefield microscopy [35].

By selectively accessing the fluorescence signals from various planes inside the sample and combining the planar images to produce three-dimensional images, this technology makes it possible to examine materials in three dimensions. A pinhole mechanism is used in CLSM to filter the fluorescence signals from the area of the sample where the laser is focused. The pinhole mechanism obstructs the fluorescence produced in the areas around the focus point. This makes it easier to create planar images by laser scanning of various locations within the sample [36].

The growth of microalgae responsible for the biodeterioration of building facades in natural environments was investigated on external thermal insulation composite systems (ETICS) and clay bricks. The adhesion of biofilm which consists of a complex microbial population embedded in a polymer matrix was indirectly determined by CLSM and it clearly demonstrated that bioreceptivity of the building materials assayed is strongly affected by surface roughness and total porosity [37].

Biocompatibility of Halloysite was studied as it is important for its potential applications in polymer composites, and it is a natural product which will not add risk to the environment. Confocal micrographs were taken with a confocal scanning system and equipped with immersion objective and their Z scan and XY scans images were acquired to demonstrate internalization of nanotubes into cells and halloysite toxicity and visualized the process of cell uptake of fluorescently labeled clay nanotubes [38].

A polymer composite based on tetra-n-butylammonium bromide (TBAB hydrate), poly (vinyl alcohol), and halloysite clay nanotubes for the cold storage were studied as both halloysite clay nanotubes and poly(vinyl alcohol) cryogel are biocompatible, and encapsulation of tetra-n-butylammonium bromide hydrate in such material will protect the environment from harmful effects of a quaternary ammonium salt and expand the scope of this cold accumulator. The structure of the cryogel samples was studied by confocal microscope and the distribution of Hal, however, could be revealed only by the confocal micrograph [39].

Polymer-driven flocculation of suspended particulate is a commonly used technique in applications such as water treatment. Wilkinson investigated the effects of complexities of polymer flocculation toward improving reagent polymer dosing [40]. An inorganic clay, bentonite, having large water absorption capacity, was used. Confocal laser scanning microscopy was used to examine the internal floc structure. It was observed that when the aggregate size remains relatively constant, the internal floc structure also remains constant, regardless of pH. These results can be used for optimization of applications.

2.5 X-Ray Techniques

2.5.1 X-Ray Tomography

Over the past years, X-Ray computed tomography has been a well-established technique in modern characterization. This technique is widely used in medical applications; however, it is expanding to other fields in polymer research as well, mainly in the applications of three-dimensional volume representation and quantitative material analysis of ceramics and composites.

The basic principle of X-Ray CT is that the sample is placed between an X-Ray source and a detection device, and projective images are recorded from various angular positions. X-Rays directed at the image from multiple orientations, decrease in intensity along the paths. This decrease is then characterized by Beer's Law, which describes intensity reduction as a function of the energy, path length, and material linear attenuation coefficient. These factors are then used to construct the distribution of X-Ray attenuation in the volume being imaged.

Eiler investigated the water diffusion in polymer composites [41]. Through the imaging of X-Ray micro-CT, they examined the internal structure of the polymer composite and calculated the inter-particular distance. The individual hydrogel particles were visualized before and after incorporation to the polymer matrix, and effective particle volume fractions were obtained. This study can be extended to numerous other applications.

Soil scientists have also been seen to use X-Ray CT to characterize soils, their 3D structures and pore networks [42]. This feature can be extended to polymer composites in this field due to the nondestructive imaging ability that this technique offers.

2.6 Other Characterization Techniques of Interest

2.6.1 X-Ray Diffraction

X-Ray diffraction is a powerful nondestructive technique for mineral characterization with a wide array of applications in many fields. X-Ray diffraction is based on the occurrence of constructive interference between monochromatic X-Rays and a crystalline sample. The law that governs this occurrence, Braggs' Law, relates the wavelength of electromagnetic radiation with the lattice spacing of the crystal. X-Rays pass through the sample, and these diffract when passing through the lattice. These diffracted rays are detected and counted throughout the directions of the lattice.

Polymers are highly crystalline, semi-crystalline, micro crystalline or amorphous and sometimes can be a combination of more than one of these forms. The final properties of the polymer depend on this form, and this can be identified by XRD analysis.

XRD is generally used to identify unknown crystalline materials. Further extension of its basic applications includes characterization of crystals, identification of fine-grained minerals, determination of unit cell dimensions, and measurement of sample purity. It presents direct evidence of the intercalation of polymer chains to clays, and is useful in analyzing phase, unit cell, crystal arrangement, spacing of atomic layers [43]. XRD is also useful in determining the degree of intercalation and exfoliation of clay into the polymer.

Knowledge about the atomic number and atomic position within the cell is determined by diffraction peak intensity, while diffraction peak position provides information about the size and shape of the unit cell [44]. Measurements are carried out in angstroms (equivalent to 0.1 nm).

Proper sample preparation is vital in analyzing a specimen by XRD, especially in materials like soils and clays which have finely divided colloids which are poor reflectors of X-Rays as well as other materials that can make X-Ray diffraction difficult [45]. Sample preparation should be conducted to remove contaminants, while obtaining the proper particle size, orientation, thickness, and other parameters. Specimens being fine grained is essential for minimal noise, as well as to ensure proper diffraction.

XRD is advantageous in terms of its non-destructivity, fast and easy sample preparation, ability in characterizing crystalline and amorphous materials, high accuracy for d-spacing calculations. However, XRD can require large amounts of sample and be time consuming.

The phenomena of intercalation and exfoliation can be identified through an analysis of the XRD spectrum. Considering the basal interlayer spacing after mixing the components, and if all the peaks do exist, it can be concluded that intercalation has occurred [13, 43]. Exfoliation is shown through very weak or missing peaks in the spectrum, indicating that the clay is fully dispersed in the polymer matrix [43]. A similar analysis was done in a study of water and nutrient absorption [8] where reactions between the clay and polymer were derived by how various peaks shifted and disappeared with intercalation and exfoliation. These properties gave further information as to the variations factors such as water absorption and nutrient release rates.

Ludeuna [13] used the interlayer spacing to conclude on the degree of intercalation, and thereby the clay dispersion degree. This was used to reveal data on mechanical and barrier properties.

Mandal [7] used XRD imaging to indicate the presence of impurities. Analysis of characteristic peaks of various compounds were used to derive information on exfoliation, dispersion, etc.

A superabsorbent preparation for absorbing nutrients and water was synthesized [12]. Typically, these superabsorbent are hydrophilic polymers, but they have low physical strength and are unsuitable for saline containing soils, so they can be intercalated with soil clays for better performance. The width of the XRD peak was used to calculate the thickness of the clays. Reactions between clay and polymer were analyzed. The peak location before and after the interaction gives an indication as to how reactions have been carried out. This paper too showed through XRD analysis whether intercalation had occurred or whether it was a surface reaction. This was attributed to the structure and reactivity differences of the clays. When the typical diffractive peak disappeared after the reaction, it could be concluded that intercalation had occurred. This information is useful to gain an insight into how further modifications could be done in the clays to get the required outputs.

El-Zahhar synthesized a polymeric composite with kaolin as a dye absorbent for the treatment of wastewater [46]. XRD was used to observe the intercalation of the polymer in kaolin by the peak shifts and decreased peaks in the composite spectrum.

2.6.2 IR Spectroscopy

Application areas for infrared spectroscopy (IR) include identifying chemical species, determining chemical species quantitatively or qualitatively, and determining molecular structure. Utilizing this method, scientists can examine matter in its solid, liquid, and gaseous phases [47].

By exposing a sample to IR light and tracking which wavelengths and to what extent they are absorbed, IR spectroscopy can determine the vibrational spectrum of that material. Since the quantity of molecules in a sample affects how much energy is absorbed, IR spectroscopy can yield both qualitative and quantitative data. Hence, chemical compound's IR spectrum is arguably its most distinctive physical characteristic, IR spectroscopy has several uses in detecting compounds and their corresponding quantities [48].

Sample preparation and safety strategies must be used for gas phase/liquid phase analysis of any sample to obtain a high-quality spectrum of the sample. Avoiding water and CO_2 absorption from the environment within the range of a typical investigation is a significant issue for the ordinary functioning of IR analysis. This issue is largely alleviated with the aid of double-beam equipment and humidity-controlled room conditions [47].

Pure clays and polymer nanocomposites are only two examples of the diverse materials that have been thoroughly characterized using infrared (IR) spectroscopy throughout the years. In case of clay, the IR analysis appeared to be complicated due to the silicon–oxygen stretching vibrational modes and $Si–O^-$ bonds. However, for clay polymer composites IR analysis is used to study the interaction between clay surfaces and polymer chains [15].

Foroutan and his team applied Fourier-transform infrared spectroscopy (FTIR) to identify the functional groups before and after adsorption of arsenic in Iranian natural clay and clay/Fe–Mn composite as-prepared to remove toxic arsenic from the liquid environment. The results showed peaks due to tensile vibrations of OH (Al–OH or deformation of the H_2O molecule), asymmetric Si–O–Si, Si–O–Al, and Si–O–Mg tensile vibrations and SiO-flexural vibrations and also revealed similar changes in both clay and composite after the adsorption of arsenic ions due to interactions between functional groups of the adsorbent and the contaminant ions [18].

An investigation on preparation of Modified Ball clay (MBC) and chitosan composite (MBC–CH) and their application for methylene blue (MB) adsorption from aqueous solution in an industrial prototype fixed-bed column adsorption revealed that MBC–CH is a potential adsorbent for cationic dye pollution remediation. FTIR spectra of MBC and MBC–CH before and after adsorption of MB revealed that the presence of more functional groups on MBC–CH composite contributed to the faster and higher adsorption process [49].

Nanoclay filled composite hydrogels showed high adsorption capacity and removal percentage of congo red (CR) and methyl violet (MV) dye from water. The hydrogel samples were characterized by FTIR using KBr pellet which was prepared in a mold by mixing dry KBr powder with fine powder of the hydrogel samples. All the shifting and overlapping signified the strong electrostatic interaction amongst the various functional groups of the hydrogels and the fillers [50].

Wang and his team recorded FTIR spectra in the transmittance mode and in the range of 500–4000 cm^{-1} at a resolution of 4 cm^{-1} for prepared montmorillonite (MMT) modified with chitosan to remove heavy metal cations by using Co^{2+} as a model ion. The intense new peaks in the composite sample indicated the strong interactions present in Chitosan–MMT [51].

2.6.3 Raman Spectroscopy

Raman spectroscopy is based on the Raman effect, which states that when molecules in a sample are excited by incoming light with a wavelength between 750 and 850 nm, the molecules will reflect light with a different wavelength. The wavelength of the reflected light enables the identification and discrimination of the chemical components in the sample [52].

Nanoclay and nanocomposites are studied by Raman spectroscopy to provide information about molecular vibrations, which are specific to the chemical bonds and symmetry of molecules. This kind of information can be used for sample identification as well as to determine the phase composition.

Titanium dioxide nanoparticles (TiO_2) can eliminate organic pollutants from air, as well as from wastewater. An investigation on anchoring TiO2 particles tightly to a suitable type of matrix to eliminate photocatalytic activity of TiO_2 and environmental risk due to the mobility of nanoparticles were used Raman spectroscopy to identify characteristic anatase bands [53].

When utilized in the microscope mode, Raman spectroscopy is particularly effective at characterizing the interactions between the constituents of polymer composites and blends. A study on the polyaniline/montmorillonite clay (PANI-MMT) system, which utilized natural clay ingredients and a water-based polymerization approach to address concerns regarding environmental and health issues, has demonstrated this. Here, Raman spectroscopy is used to investigate how the amount of MMT in the nanocomposite changes over time, changing the delicate interactions between MMT and intercalated PANI [54].

Raman spectroscopy is a useful tool for nondestructive characterization. An investigation on building a nanomaterial to degrade or filtrate pollutants from soils, water, or air using natural clays, engineered Ag-nanoparticles (NP), TiO_2-NP, and exhausted coffee grounds used to identify the main molecular groups present in the samples. The results proved that this nanocomposite can also be used to chelate and separate other contaminants from soil or water [55].

Bentonite (BEN) clay, which mostly consists of montmorillonite, is used in a variety of applications, including environment, agriculture, pharmaceuticals, cosmetics, adsorbents to remove hazardous substances, and as a catalyst and a component in fluorescence probes with high sensitivity. Following that, Raman scattering studies were utilized to identify the structural changes present in a novel bentonite loaded CuWO4 (BEN-CuWO4) nanocomposite synthesized through hydrothermal method [56].

An investigation on the microstructure and adsorption capacity of cellulosic biomass carbon-based montmorillonite (MMT) composite as a high quality, environmental friendly renewable resource used Raman spectrum to characterize the nanocomposite and it has showed that the introduction of MMT component can enhance the surface performance also induce unavoidable damages to the ordered carbon structure [57].

3 Choosing the Right Technique

There are numerous techniques that exist which can give an interpretation of material features in various scales and precisions.

In summary, the advantages and disadvantages of the discussed imaging techniques can be listed down as shown in Table 1.

These techniques vary in their details, scope and type of output information that they give, and depending on what our focus is, the technique can vary. Considering the imaging techniques that were discussed in this chapter, and their features, choosing the relevant technique can be based on the various properties. Furthermore, several techniques can be used at once to confirm the results obtained by one technique, the results may be compared.

Table 1 Advantages and limitations of various imaging techniques

Imaging technique	Advantages	Disadvantages
Fluorescence	• Highly sensitive and specific • Good selectivity • Multidimensional character	• Dependence on probes • Can cause poor signal to noise ratio
Confocal microscopy	• Superior image clarity • Less specimen preparation • Can provide 3D images • Capable of visualizing internal structure	• Poor resolution • Limited number of excitation wavelengths
SEM	• Examines very large area	• Cannot image wet samples
TEM	• Provides atomic scale resolution	• Long and sophisticated sample preparation techniques • Expensive • Limited areal coverage • Require high vacuum • Project a 3D object onto a 1D plane
AFM	• Provides a 3D profile • Works in ambient air • High resolution • cost-effective microscope for nanoscale imaging • less laboratory spaces • Does not require a specially trained operator	• Single scan image size is less • Scanning speed is low
NMR	• Nondestructive • Easy sample preparation • Require small sample volumes	• Expensive • Not suitable for molecules of higher molecular weight • Only nuclei having magnetic moments can be analyzed
XRD	• Nondestructive • Easy sample preparation • Easy interpretation of data • Availability	• Requires large volume of sample • Time consuming
Raman	• No sample preparation needed • Not interfered by water • Nondestructive • Many organic and inorganic materials are suitable for analysis • Spectra can be collected from a very small volume	• Detection needs a sensitive and highly optimized instrumentation • Fluorescence of impurities can hide the Raman spectrum
IR	• Gases, solids, and liquids can be analyzed • Nondestructive technique • High resolution, fast technique	• Complicated to analyze samples that contain water • Require very sensitive and properly tuned devices

4 Prospects of Imaging Techniques of Clay Composites

With the development of technology and the requirement for faster and more efficient characterization, better techniques are now available that offer superior features. These may be more costly; however, they are more focused toward the work in hand. These emerging techniques have not been discussed in detail in this chapter; the reader is directed to further references in order to get a better idea of these techniques.

Newer and more advanced equipment are now available that present easier and faster imaging and characterization. The conventional SEM (CSEM), the variable pressure SEM (VPSEM), and the environmental SEM (ESEM) [58] are a few of the variants of the SEM that are now available. These equipment are versatile in their features such as no sample preparation, lower required voltage, time resolved imaging, and much more. SEM provides grayscale images since the images are formed from electrons. However, there are modern techniques [59] that offer both 2D and 3D color images of the SEM results by various modifications done to the obtained result. These offer better interpretation of the results.

Generally, AFM images can be affected by the hysteresis of the piezoelectric material and interactions between axes that may require software enhancement and filtering [60]. These filtering flattens out real topographical features. Newer AFMs consist of closed-loop scanners which helps eliminate this problem.

In comparison to elastically scattered photons and the strong fluorescence background, the percentage of Raman scattered photons are very low. This can completely hide the Raman peaks and therefore detection needs a highly sensitive instrumentation. Various techniques are now available that overcome these issues namely the Confocal Raman Spectroscopy (CRS), Modulated Raman Spectroscopy (MRS), Surface-Enhanced Raman Spectroscopy (SERS), and Tip-Enhanced Raman Spectroscopy (TERS) [61].

5 Conclusions

The development of clay polymer composites is on the rise, with an increasing arena of applications in numerous fields. The incorporation of a small amount of clay in a polymer matrix enhances the properties of the composite with respect to the initial constituents and these can be advantageous in terms of properties such as mechanical, thermal, electric barriers, electrical conductivity, water absorption. In the journey of preparing such composites, or enhancing those that exist, it is vital to know an in-depth analysis of the materials, their formation, structure, and composition. This can aid in achieving better outputs in terms of these properties. Characterization of these composites are hence required. There is a wide range of imaging techniques that are available for evaluating the properties of composites in combination with other characterization techniques. This chapter discussed a few of the main imaging techniques related to characterization of clay polymer composites with a basic outline of the principle of operation, sample preparation, analysis and their advantages and limitations. Furthermore, factors that would be helpful in selecting the suitable technique were also highlighted.

References

1. Beall, G.W., Powell, C.E.: Engineering properties of polymer—Clay nanocomposites theory and theory validation. In: Fundamentals of Polymer-Clay Nanocomposites, pp. 49–67. Cambridge University Press (2011)
2. Shunmugasamy, V.C., Xiang, C., Gupta, N.: Clay/polymer nanocomposites: Processing, properties, and applications. In: Hybrid and Hierarchical Composite Materials, pp. 161–200. Springer International Publishing (2015)
3. Anadao, P.: Polymer/clay nanocomposites: concepts, researches, applications and trends for the future. In: Nanocomposites—New Trends and Developments. InTech (2012)
4. Iturrondobeitia, M., Guraya, T., Okariz, A., Srot, V., van Aken, P.A., Ibarretxe, J.: Quantitative electron tomography of PLA/clay nanocomposites to understand the effect of the clays in the thermal stability. J. Appl. Polym. Sci. **134**, (2017). https://doi.org/10.1002/app.44691
5. Cavallaro, G., de Lisi, R., Lazzara, G., Milioto, S.: Polyethylene glycol/clay nanotubes composites: thermal properties and structure. J. Therm. Anal. Calorim. 383–389 (2013)
6. Saurabh, K., Kanchikeri Math, M., Datta, S.C., Thekkumpurath, A.S., Kumar, R.: Nanoclay polymer composites loaded with urea and nitrification inhibitors for controlling nitrification in soil. Arch. Agron. Soil Sci. **65**, 478–491 (2019). https://doi.org/10.1080/03650340.2018.1507023
7. Mandal, N., Datta, S.C., Manjaiah, K.M., Dwivedi, B.S., Kumar, R., Aggarwal, P.: Zincated nanoclay polymer composites (Zncpcs): synthesis, characterization, biodegradation and controlled release behaviour in soil. Polym. Plast. Technol. Eng. **57**, 1760–1770 (2018). https://doi.org/10.1080/03602559.2017.1422268
8. Mukhopadhyay, R., De, N.: Nano clay polymer composite: synthesis, characterization, properties and application in Rainfed agriculture synthesis of chitosan grafted nanoclay potassium fertilizer and its effect on alfalfa view project chemical compostion of essential oil of excoecaria acerifolia view project (2014)
9. Raval, N., Maheshwari, R., Kalyane, D., Youngren-Ortiz, S.R., Chougule, M.B., Tekade, R.K.: Importance of physicochemical characterization of nanoparticles in pharmaceutical product development. In: Basic Fundamentals of Drug Delivery, pp. 369–400. Elsevier (2019)
10. Sciau, P.: Transmission electron microscopy emerging investigations for cultural heritage materials. In: Advances in Imaging and Electron Physics, pp. 43–67. Academic Press Inc. (2016)
11. Monticelli, O., Musina, Z., Russo, S., Bals, S.: On the use of TEM in the characterization of nanocomposites. Mater. Lett. **61**, 3446–3450 (2007). https://doi.org/10.1016/j.matlet.2006.11.086
12. Sarkar, S., Datta, S.C., Biswas, D.R.: Synthesis and characterization of nanoclay-polymer composites from soil clay with respect to their water-holding capacities and nutrient-release behavior. J. Appl. Polym. Sci. **131** (2014). https://doi.org/10.1002/app.39951
13. Ludueña, L.N., Vázquez, A., Alvarez, V.A.: Effect of the type of clay organo-modifier on the morphology, thermal/mechanical/impact/barrier properties and biodegradation in soil of polycaprolactone/clay nanocomposites. J. Appl. Polym. Sci. **128**, 2648–2657 (2013). https://doi.org/10.1002/app.38425
14. Farré, M., Barceló, D.: Introduction to the analysis and risk of nanomaterials in environmental and food samples. In: Comprehensive Analytical Chemistry, pp. 1–32 (2012)
15. Sinha Ray, S.: Structure and morphology characterization techniques. In: Clay-Containing Polymer Nanocomposites, pp. 39–66 (2013)

16. Cascione, M., Matteis, V.D., Persano, F., Leporatti, S.: AFM Characterization of Halloysite clay nanocomposites' superficial properties: current state-of-the-art and perspectives. Materials. **15**, 1–12 (2022)
17. Shokri, E., Yegani, R., Pourabbas, B., Kazemian, N.: Preparation and characterization of polysulfone/organoclay adsorptive nanocomposite membrane for arsenic removal from contaminated water. Appl Clay Sci. **132–133**, 611–620 (2016). https://doi.org/10.1016/j.clay.2016.08.011
18. Foroutan, R., Mohammadi, R., Adeleye, A.S., Farjadfard, S., Esvandi, Z., Arfaeinia, H., Sorial, G.A., Ramavandi, B., Sahebi, S.: Efficient arsenic(V) removal from contaminated water using natural clay and clay composite adsorbents. Environ. Sci. Pollut. Res. **26**, 29748–29762 (2019). https://doi.org/10.1007/s11356-019-06070-5
19. Bhagyaraj, S., Krupa, I.: Alginate—Halloysite nanocomposite aerogel: preparation, structure, and oil/water separation applications. Biomolecules **10**, 1–16 (2020). https://doi.org/10.3390/biom10121632
20. Matusik, J., Stodolak, E., Bahranowski, K.: Synthesis of polylactide/clay composites using structurally different kaolinites and kaolinite nanotubes. Appl. Clay Sci. **51**, 102–109 (2011). https://doi.org/10.1016/j.clay.2010.11.010
21. Grandjean, J.: Solid-state NMR study of modified clays and polymer/clay nanocomposites
22. Chatham, J.C., Blackband, S.J.: Nuclear magnetic resonance spectroscopy and imaging. Animal Res. ILAR J. **42**, 189–208 (2001). https://doi.org/10.1093/ilar.42.3.189
23. Huang, W., Liu, Z., Zhou, C., Yang, X.: Enhancement of Soil Ecological Self-Repair using a Polymer Composite Material. Catena (Amst). **188** (2020). https://doi.org/10.1016/j.catena.2019.104443
24. Huang, W., Du, J., Sun, H., Zhou, C., Liu, Z., Zhang, L.: New polymer composites improve silty clay soil microstructure: an evaluation using NMR. Land Degrad. Dev. **32**, 3272–3281 (2021). https://doi.org/10.1002/ldr.3983
25. Bouznik, V.M., Morozov, E.V., Avilova, I.A., Volkov, V.I.: NMR applications for polymer composite materials moisture uptake investigation. Appl. Magn. Reson**47**, 321–334 (2016). https://doi.org/10.1007/s00723-015-0748-2
26. Huang, W., Du, J., Sun, H., Zhou, C., Liu, Z., Zhang, L.: New polymer composites improve silty clay soil microstructure: an evaluation using NMR. Land Degrad Dev. **32**, 3272–3281 (2021). https://doi.org/10.1002/ldr.3983
27. Sanderson, M.J., Smith, I., Parker, I., Bootman, M.D.: Fluorescence microscopy. Cold Spring HarbProtoc. **2014**, 1–36 (2016). https://doi.org/10.1101/pdb.top071795.Fluorescence
28. Aloisi, G.G., Elisei, F., Nocchetti, M., Camino, G., Frache, A., Costantino, U., Latterini, L.: Clay based polymeric composites: preparation and quality characterization. Mater Chem Phys. **123**, 372–377 (2010). https://doi.org/10.1016/j.matchemphys.2010.04.020
29. Sikorska, E.: Fluorescence spectroscopy and chemometrics in analysis of beverages. Elsevier Inc. (2019)
30. Nguyen, T.P., Yang, S.H.: Hybrid materials based on polymer nanocomposites for environmental applications. Elsevier Ltd. (2018)
31. Dodoo-Arhin, D., Dodoo-Arhin, D., Konadu, D.S., Annan, E., Buabeng, F.P., Yaya, A., Agyei-Tuffour, B.: Fabrication and characterisation of ghanaian bauxite red mud-clay composite bricks for construction applications. Am. J. Mater. Sci. **2013**, 110–119 (2013). https://doi.org/10.5923/j.materials.20130305.02
32. Ahmadi, M.F., Rusling, J.F.: Fluorescence studies of solute microenvironment in composite clay-surfactant films. Langmuir **11**, 94–100 (1995). https://doi.org/10.1021/la00001a019
33. Wu, L., Bao, X., Zhong, H., Pan, Y., Lv, G., Liao, L.: Preparation of a novel clay/dye composite and its application in contaminant detection. Clays Clay Miner. **67**, 244–251 (2019). https://doi.org/10.1007/s42860-019-00022-3
34. Premarathna, K.S.D., Rajapaksha, A.U., Adassoriya, N., Sarkar, B., Sirimuthu, N.M.S., Cooray, A., Ok, Y.S., Vithanage, M.: Clay-biochar composites for sorptive removal of tetracycline antibiotic in aqueous media. J. Environ. Manag. **238**, 315–322 (2019). https://doi.org/10.1016/j.jenvman.2019.02.069

35 Canette, A., Briandet, R.: Microscopy: confocal Laser Scanning Microscopy. Elsevier (2014)
36. Prabhakaran, P., Kim, T.D., Lee, K.S.: Polymer Photonics. Elsevier B.V. (2012)
37. D'Orazio, M., Cursio, G., Graziani, L., Aquilanti, L., Osimani, A., Clementi, F., Yéprémian, C., Lariccia, V., Amoroso, S.: Effects of water absorption and surface roughness on the bioreceptivity of ETICS compared to clay bricks. Build. Environ. **77**, 20–28 (2014). https://doi.org/10.1016/j.buildenv.2014.03.018
38. Tarasova, E., Naumenko, E., Rozhina, E., Akhatova, F., Fakhrullin, R.: Cytocompatibility and uptake of polycations-modified halloysite clay nanotubes. Appl. Clay Sci. **169**, 21–30 (2019). https://doi.org/10.1016/j.clay.2018.12.016
39. Stoporev, A., Mendgaziev, R., Artemova, M., Semenov, A., Novikov, A., Kiiamov, A., Emelianov, D., Rodionova, T., Fakhrullin, R., Shchukin, D.: Ionic clathrate hydrates loaded into a cryogel—Halloysite clay composite for cold storage. Appl. Clay Sci. **191**, 105618 (2020). https://doi.org/10.1016/j.clay.2020.105618
40. Wilkinson, N., Metaxas, A., Quinney, C., Wickramaratne, S., Reineke, T.M., Dutcher, C.S.: pH dependence of bentonite aggregate size and morphology on polymer-clay flocculation. Colloids Surf. A Physicochem. Eng. Asp. **537**, 281–286 (2018). https://doi.org/10.1016/j.colsurfa.2017.10.007
41. Eiler, J., Simonsen, S.B., Hansen, D., Bingöl, B., Hansen, K., Thormann, E.: Water transport in polymer composites through swelling-induced networks of hydrogel particles. Soft Matter. **16**, 8254–8261 (2020). https://doi.org/10.1039/D0SM01103G
42. Schlüter, S., Sammartino, S., Koestel, J.: Exploring the relationship between soil structure and soil functions via pore-scale imaging. Geoderma **370**, 114370 (2020). https://doi.org/10.1016/j.geoderma.2020.114370
43. Das, P., Manna, S., Behera, A.K., Shee, M., Basak, P., Sharma, A.K.: Current synthesis and characterization techniques for clay-based polymer nano-composites and its biomedical applications: a review. Environ. Res. **212** (2022). https://doi.org/10.1016/j.envres.2022.113534
44. Ali, A., Chiang, Y.W., Santos, R.M.: X-ray diffraction techniques for mineral characterization: a review for engineers of the fundamentals. Appl. Res. Direct. Miner. **12** (2022). https://doi.org/10.3390/min12020205
45. Bunaciu, A.A., Udriştioiu, E. gabriela, Aboul-Enein, H.Y.: x-ray diffraction: instrumentation and applications. Crit. Rev. Anal. Chem. **45**, 289–299 (2015). https://doi.org/10.1080/10408347.2014.949616
46. El-Zahhar, A.A., Awwad, N.S., El-Katori, E.E.: Removal of bromophenol blue dye from industrial waste water by synthesizing polymer-clay composite. J. Mol. Liq. **199**, 454–461 (2014). https://doi.org/10.1016/j.molliq.2014.07.034
47. Ghosh, S.N.: Handbook of analytical techniques in concrete science and technology. In: Handbook of Analytical Techniques in Concrete Science and Technology, pp. 174–204 (2001)
48. Albert, D.E.: Methods for verifying medical device cleanliness. In: Developments in Surface Contamination and Cleaning, pp. 109–128. Elsevier Inc. (2015)
49. Auta, M., Hameed, B.H.: Chitosan-clay composite as highly effective and low-cost adsorbent for batch and fixed-bed adsorption of methylene blue. Chem. Eng. J. **237**, 352–361 (2014). https://doi.org/10.1016/j.cej.2013.09.066
50. Bhattacharyya, R., Ray, S.K.: Removal of congo red and methyl violet from water using nano clay filled composite hydrogels of poly acrylic acid and polyethylene glycol. Chem. Eng. J. **260**, 269–283 (2015). https://doi.org/10.1016/j.cej.2014.08.030
51. Wang, H., Tang, H., Liu, Z., Zhang, X., Hao, Z., Liu, Z.: Removal of cobalt(II) ion from aqueous solution by chitosan-montmorillonite. J. Environ. Sci. (China) **26**, 1879–1884 (2014). https://doi.org/10.1016/j.jes.2014.06.021
52. Synetos, A., Tousoulis, D.: Invasive imaging techniques. In: Coronary Artery Disease: from Biology to Clinical Practice, pp. 359–376. Elsevier Inc. (2017)
53. Peikertová, P., Rebilasová, S., Gröplová, K., Neuwirthová, L.: Raman study of clay/TiO_2 COMPOSITES. In: Nanocon, p. 5 (2011)
54. Shakoor, A., Rizvi, T.Z., Nawaz, A.: Raman spectroscopy and AC conductivity of polyaniline montmorillonite (PANI-MMT) nanocomposites. J. Mater. Sci.: Mater. Electron. **22**, 1076–1080 (2011). https://doi.org/10.1007/s10854-010-0262-0

55. Urdapilleta-Inchaurregui, V., Fernández-Luqueño, F., Torres-Huerta, A.M., Roa-Velázquez, D., Rodríguez-Varela, F.J., Sánchez-Castro, M.E.: Nanocomposite synthesis from a natural clay-rich soils and exhausted coffee grounds for environmental applications. J. Nano Res. **63**, 47–63 (2020). https://doi.org/10.4028/www.scientific.net/JNanoR.63.47
56. Thiruppathi, M., Selvakumar, K., Arunpandian, M., Thirumalai, K., Ramalingan, C., Swaminathan, M., Nagarajan, E.R.: An affordable photocatalyst for pharmaceuticals and superior electrocatalyst for methanol oxidation—A dual role by CuWO4 anchored bentonite clay. Colloids Surf. A Physicochem. Eng. Asp. **563**, 148–159 (2019). https://doi.org/10.1016/j.colsurfa.2018.12.006
57. Yang, X., Li, F., Xia, M., Luo, F., Jiang, Y.: Investigation on the micro-structure and adsorption capacity of cellulosic biomass carbon based montmorillonite composite. Microporous Mesoporous Mater. **256**, 18–24 (2018). https://doi.org/10.1016/j.micromeso.2017.07.052
58. Zankel, A., Nachtnebel, M., Mayrhofer, C., Wewerka, K., Müllner, T.: Characterisation of polymers in the scanning electron microscope—From low-voltage surface imaging to the 3D reconstruction of specimens. In: Springer Series in Materials Science, pp. 95–108. Springer Verlag (2017)
59. Mignot, C.: Color (and 3D) for scanning electron microscopy. Micros. Today **26**, 12–17 (2018). https://doi.org/10.1017/s1551929518000482
60. Babu, R., Singh, E.: Atomic force microscopy: a source of investigation in biomedicine. Int. J. Electron. Electr. Eng. **7**, 59–66 (2014)
61. Adya, A.K., Canetta, E.: Nanotechnology and its applications to animal biotechnology. In: Animal Biotechnology, pp. 247–263. Elsevier (2014)

Enriched Clay-Polymer Composites and Their Applications

**Dinusha Peramune, Pamoda Peduruhewa, Sachira Hewawardhana,
W. P. Yashodhara Perera, H. H. P. B. Sandaruwan,
Danushika C. Manatunga, and Rohan S. Dassanayake**

Abstract Clay-polymer composites are formed by amalgamating two components with mineral and organic pedigrees. Enriched clay-polymer composites have recently attracted tremendous attention due to the synergetic effects arising from the individual polymer and clay constituents. In addition, clays show enhanced intercalation properties and compatibility with natural and synthetic polymers. As a result, there is a growing interest in academia and industry in developing advanced and smart composite materials. Enriched clay-polymer composites have been commonly considered in numerous applications as they exhibit significant improvements in the mechanical, thermal, biodegradability, nontoxicity, barrier, carrier, and sorption properties. This chapter provides an overview of the recent applications of enriched clay-polymer composites in contaminant removal, flame retardancy, food packaging, antimicrobial, drug delivery, and other medical applications.

1 Introduction

Clays are ubiquitous, environmentally benign, and low-cost earthy minerals generated due to the weathering and erosion of rocks over an extended period of time. Raw clay deposits are primarily composed of two or more clay minerals mixed with non-clay materials in the form of associate minerals, including feldspar, quartz, carbonates, oxides, and hydrated oxides, along with organic matter and amorphous substances [1, 2]. In numerous applications, clays are directly used from the deposit

---

D. Peramune · P. Peduruhewa · S. Hewawardhana · D. C. Manatunga · R. S. Dassanayake (✉)
Department of Biosystems Technology, Faculty of Technology, University of Sri Jayewardenepura, Pitipana, Homagama 10200, Sri Lanka
e-mail: rdassanayake@sjp.ac.lk

W. P. Y. Perera
Sri Lanka Institute of Nanotechnology, Nanotechnology and Science Park, Pitipana, Homagama 10200, Sri Lanka

H. H. P. B. Sandaruwan
Department of Chemistry, Faculty of Science, University of Ruhuna, Matara 81000, Sri Lanka

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_13

without any separation or enrichment of the clay minerals [3]. However, the enrichment of clays is imperative, especially in environmental and biomedical applications. Size fractionation is the most widely used technique to enrich clay minerals from non-clay materials [3]. This technique can also be used to separate and isolate different types of clay in the raw clay deposit [3]. Commonly applied size fractionation techniques include centrifugation, filtration, and sedimentation [4]. Additionally, ultrasonication and magnetic treatments are also employed for clay enrichment [4].

Polymer composites are multi-phase materials where reinforcing constituents are embedded with the polymer matrix, resulting in synergistic properties that differ from individual components present in the composite. Polymer composites inherit distinctive characteristics such as high mechanical and chemical, lightweight, electrical, thermal, and optical properties. Clays have been employed as reinforcing fillers for polymer composites due to their relative abundance, excellent compatibility, and intercalation ability with polymers, giving rise to clay-polymer composites or organoclays [5].

Interestingly, enriched clay-polymer composites have been tremendously improved and applied commercially in recent years. Those composites possess unique features, including stiffness, barrier properties, thermal and flame resistance, flexibility, nontoxicity, biocompatibility, superhydrophobicity, high mechanical properties, and resistance to hydrolysis. Therefore, they have been widely employed in environmental, food and medical applications. This chapter focuses on the recent applications of enriched clay-polymer composites in water remediation, mainly dye, pesticides, pharmaceuticals and phenolic contaminants and heavy metal removal, food packing, fire retardants, and medical fields: antimicrobial agents, drug delivery, and other biomedical applications.

2 Wastewater Remediation Applications

Among many water remediation techniques, the adsorption process by solid adsorbents is considered one of the most efficient and effective techniques due to its simplicity, low cost, and sustainability [6]. Over the last few years, enriched clay-polymer composites have emerged as a novel technology for removing contaminants from wastewater since clay particles and polymers possess excellent adsorption abilities [7]. This section covers the utilization of clay-polymer composites in the dye, pesticides, pharmaceuticals and phenolic contaminants and heavy metal removal applications.

2.1 Dye Removal

Studies have been conducted to discover the adsorption capacities and dye removal efficiencies of enriched clay-polymer composites developed using different clay materials and polymers. Table 1 summarizes the dye removal efficiencies and adsorption capacities of several key enriched clay-polymer composites studied over the last five years.

Compared to the polymer adsorbents, the dye adsorption enhancement of enriched clay-based adsorbents is mainly driven by the porous structure and the increased surface area provided by the clay constituent of the composite. Several studies have reported high surface areas and pore volumes in enriched clay-polymer composites due to the scattering of clay minerals on polymer matrices, enlarging their surfaces

Table 1 Comparison of dye removal by various enriched clay-polymer composites

Composite	Contaminant	Removal efficiency (%)	Adsorption capacity (mg/g)	Isotherm	Ref
Amine-modified clay-enriched chitosan/ alginate	Acid black-172 Methylene blue	78.15 71.51	71.5	–	[11]
Bentonite/polyaniline/Ni_2O_3	Safarnin-O	100/ 300 min	–	–	[12]
Lanthanum (III) incorporated chitosan-montmorillonite	Reactive red	90.5/ 40 min	39.32	Langmuir	[10]
Montmorillonite supported-poly (acrylamide-co-acrylic acid) hydrogel	Methylene blue	97/20 min	717.5	Sips	[13]
Zr (IV) encapsulated carboxymethyl cellulose-montmorillonite	Reactive red	96.5%/ 40 min	39.33	Langmuir	[8]
Polyvinyl alcohol/sodium alginate/ ZSM-5 zeolite membrane	Congo red	99.9	4.8	Freundlich	[14]
Zeolite-Y incorporated karaya gum hydrogel	Brilliant green	98.8	1461.35	Langmuir	[15]
κ- carrageenan-poly (acrylamide-co-methacrylic acid)/ AQSOA-Z05 zeolite hydrogel	Methylene blue	99	682.15	Langmuir	[16]
Lanthanum (III) supported carboxymethylcellulose-clay composite	Indigo carmine Acid blue Reactive blue 4	80.41/ 60 min 83.54/ 60 min 86.91/ 60 min	40.11 42.45 43.65	Freundlich	[9]
Crosslinked chitosan-tripolyphosphate/ kaolin clay composite	Remazol brilliant blue	99.5	687.2	Langmuir	[17]

[8–10]. Khan et al. investigated this phenomenon and reported over 75% increase in the adsorption capacity in amine-modified clay-enriched chitosan/alginate aerogel compared to pure chitosan. This is justified by the superior porous structure of the freeze-dried triple network aerogel than chitosan, alginate, and modified clay [11]. Another study conducted by Sirajudheen et al. showed the adsorption of the negatively charged reactive red dye molecules onto protonated amine groups (NH_3^+) of chitosan and the positively charged La^{3+} and Al^{3+} in the composite [10]. The hydrogen bonding between free hydroxyl groups of the composites and the nitrogen and oxygen centers in dye molecules also involves dye adsorption [10].

2.2 Pesticides, Pharmaceuticals and Phenolic Contaminants Removal

Besides organic dye effluents, other organic effluents in industrial wastewater, such as pesticides, pharmaceuticals, phenolics and organic acids, can also be harmful. Therefore, numerous studies have been conducted on removing other organic pollutants using enriched clay-polymer composites. Table 2. summarizes the removal of organic contaminates using enriched clay-polymer composites reported in the literature. However, as opposed to organic dye adsorption applications, only limited studies have been conducted on removing other organic pollutants using clay-polymer composites.

2.3 Heavy Metal Removal

Heavy metals, including arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), thallium (Tl), and zinc (Zn) are one of the main inorganic pollutants that can be found in industrial effluents. Heavy metals can be extremely hazardous for humans, living stocks, and aqua life forms due to their high toxicity, carcinogenicity, and bioaccumulation. Thus, studying and developing novel, eco-friendly, cost-effective heavy metal removal techniques need immediate attention. Due to their enhanced adsorption properties, enriched clay-polymer composites are considered favorable candidates for heavy metal removal. However, the polymer component of the clay-polymer composite is predominantly responsible for heavy metal ion adsorption.

Cation retention capacity is an essential factor in heavy metal removal adsorbents as it determines the adsorption capacity of the composite. For example, Manjaiah et al. developed a chitosan-g-poly (acrylic acid)-bentonite composite with a higher cation retention capacity of 95.5 cmol (p^+) kg^{-1} than that of 83.3 cmol (p^+) kg^{-1} for pure bentonite [22]. The modified clay-polymer composite showed enhanced cation

Table 2 Removal of pesticides, pharmaceuticals and phenolic contaminants using enriched clay-polymer composites

Composite	Contaminant	Removal efficiency (%)	Adsorption capacity (mg/g)	Isotherm	Ref
Carboxymethyl cellulose/ modified nano organo-bentonites composite	Atrazine, butachlor, carbendazim, carbofuran, imidacloprid, iso-proturon, pendimethalin, thiophanate methyl, and thiamethoxam	57–100%	–	–	[18]
Organo-modified montmorillonite/ alginate composite	Phenol 4-chlorophenol	25 67	0.118 0.334	–	[19]
Magnetic bentonite/chitosan composite	Atenolol Ciprofloxacin Gemfibrozile	85 95 90	15.63 39.06 24.79	Dubinin-Radushkevich	[20]
Synthesized poly-4-vinyl(1-(2-hydroxyethyl)-pyridinium bromide/ montmorillonite composite	Gemfibrozile	80	100%	–	[21]

uptake by adsorption. Moja et al. described the fabrication of chitosan/polypropylene-grafted- maleic anhydride (PP-g-MA)/MMT composite for lead removal application [23]. The heavy metal adsorption by clay-polymer composites can be improved by magnetifying the clay minerals. For example, Chen et al. reported successful heavy metal adsorption by a clay/polymer composite constructed using magnetic attapulgite and bacterial cellulose [24]. Table 3 summarizes the recent examples of heavy metal removal by enriched clay-polymer composites.

3 Food Packaging

Numerous studies on enriched clay-polymer composites are currently underway to prepare food packaging materials that act as a barrier to moisture and microbial contamination and prevent the penetration of gases such as oxygen, carbon dioxide, and other volatile compounds such as flavors and contaminants [28, 29]. Besides food safety, enriched clay-polymer composites-based packaging improves the nutritional value [30].

Clay mineral halloysite, is a strong candidate for developing clay-polymer composites to inhibit bacterial or fungal growth in food samples. The quality of

Table 3 Comparison of heavy metal removal by various enriched clay-polymer composites

Composite	Heavy metal(s) treated	Adsorption capacity (mg/g)	Removal efficiency (%)	Isotherm	Ref
Polypropylene-grafted-maleic anhydride/chitosan polymer blend functionalized with montmorillonite	Pb (II)	73.8	94	Langmuir	[23]
Polyacrylamide/ Sodium montmorillonite nanocomposite	Co (II) Ni (II)	108.69 119.05	98.67 99.30	Langmuir	[25]
Lignin xanthate resin–bentonite clay composite	Hg (II)	45	95	Langmuir	[26]
Bacterial cellulose/attapulgite magnetic composites	Pb (II) Cu (II) Cr (VI)	66.4 71.2 85.0	90/2 h	Langmuir	[24]
Chitosan-g-poly (acrylic acid)-bentonite composite	Cu (II) Zn (II) Cd (II) Ni (II)	88.5 72.9 51.5 48.5	95 95 85 70	Langmuir	[22]
Activated bentonite-alginate composite	Cu (II) Pb (II)	17.30 107.52	58 77	Langmuir	[27]
Amine-modified clay-enriched chitosan/alginate	Cr (IV)	62.4	75	–	[11]

this clay preserves the freshness of the food and can prevent bacterial or fungal attacks that cause food spoilage and food poisoning [31]. Furthermore, as explained by Yahiaoui et al. poly (e-caprolactone) (PCL)/clay composites can be used to prepare food packaging with antimicrobial properties using the melt mixing process [32]. It is also capable of inhibiting 90% of the growth of *Escherichia coli* and *Staphylococcus aureus* in the food matrix. Moreover, this modified package reduces water vapor permeability values by 56% and reduces microbial growth on food and the environmental conditions conducive to microbial growth [32]. Jafarzadeh et al. investigated the physical, mechanical, thermal, barrier, and antimicrobial properties of the nanokaolin semolina films [33]. The antibacterial properties were tested against *Staphylococcus aureus* and *Escherichia coli*. The authors reported that the inclusion of nanokaolin enhanced the barrier, mechanical, and antimicrobial properties of semolina films, indicating the potential application of these bionanocomposites in food packaging [33].

Neves et al. prepared an enriched clay-biopolymer composite using chitosan and bentonite clay for food packing application [34]. The authors reported significant improvements in the water vapor and mechanical barrier properties against vibrations and tension [34]. Moustafa and coworkers fabricated biodegradable poly (butylene adipate-co-terephthalate)/organoclay (PBAT/OC) bionanocomposites incorporating different proportions of cumin essential oil (CEO) [35]. CEO incorporated PBAT/OC films showed enhanced UV shielding and mechanical and antimicrobial properties. The authors claimed that the PBAT/OC/CEO films could be used in agriculture mulch films and light-sensitive packaging, including food and drugs [35].

4 Flame Retardant Materials

Clay-polymer composites have been widely investigated as flame retardants due to the ability of clays to reduce the flammability of the composites and enhance flame retardancy. The flame retardancy mechanism involves the formation of an inorganic–organic protective layer over the combusting material, insulating the underlying materials from the heat flux of the flame and reducing the heat transfer. Numerous clay-polymer composites have been tested as reinforcement in rubbers, leathers, and other polymers, making them less flammable [36, 37]. These flame retardant clay-polymer composites show a significant decrease in peak heat release rate, change char structure, and reduce the mass loss rate during the burning [38]. Moreover, these composites do not increase the carbon monoxide and soot produced during the burning [39]. For example, polyamide 66/montmorillonite nanocomposites and polypropylene/montmorillonite nanocomposites display excellent thermal stability and lower peak heat-releasing rate [40, 41]. Organically developed poly (lactic acid) (PLA) with melamine polyphosphate (MPP) and Cloisite 30B (C-30B) composite also showed good flame retardant properties compared to conventional flame retardant materials [42]. Polypropylene /organoclay nanocomposites, polypropylene/protonic clay nanocomposites, and polypropylene/pristine clay nanocomposites show less heat-releasing rate and good thermal stability [38].

5 Biomedical Applications

Recently, enriched clay-copolymers have gained attention in the biomedical field due to their excellent characteristics, including barrier function, biocompatibility, controlled drug release, stimuli responsiveness, antimicrobial properties, and nontoxicity. Furthermore, these composites can be processed into various morphologies such as films, fibers, scaffolds, hydrogels, and bioinks. Biomedical applications of clay-polymer composites are briefly discussed in the following section.

5.1 Antimicrobial Agents

Enriched clay-polymer composites are recently gaining popularity as antimicrobial agents due to their low toxicity, high performance, and low cost [43]. Since the metals, including chromium, zinc and copper, show antimicrobial activities against a diverse range of pathogens, enriched clay-polymer composites with such metals also exhibit excellent antimicrobial activities [44]. Based on their antimicrobial properties, enriched clay-polymer composites have been investigated in the food industry to ensure the quality and safety of various food products and to prevent the effects of microbial infections [45]. In addition to the food industry, the antimicrobial activity of clay-polymer composites has also been studied in the textiles, agriculture, paints, and cosmetics industries [46].

There is also a tendency to develop enriched clay-polymer composites using biopolymers with antimicrobial properties in agriculture-related products [35, 45]. For instance, chitosan and various clays or clay minerals, including montmorillonite, zeolite, alumina, bentonite, and laponite, have been tested to improve the bioavailability of bioactive compounds in food [31, 47]. These biopolymer-clay composites also enhance food quality and health effects and inherit distinct properties such as high biocompatibility, nontoxicity, mechanical strength, antibacterial activity, and drug loading capacity [48]. Passaretti et al. developed agricultural mulches using thermoplastic starch and mica clay [49]. The general approach of mulches is to avoid weeds and to maintain temperature, humidity, and soil structure, preventing erosion and improving water management. However, the authors reported antibacterial activity in mulches after incorporating clay-biopolymer composites [50]. Merino et al. prepared clay-biopolymer composites using native and oxidized corn starch and bentonite (Bent) and chitosan-modified bentonite (Bent-CS) fillers to be used as agricultural mulch films [51]. The composites with oxidized starch and Bent and Bent-CS showed significant antibacterial inhibition against Escherichia coli and Listeria [51]. Enriched clay-polymer composites have been employed to develop antibacterial membranes in water treatment systems [52]. For example, Ying and coworkers developed high-performance water purification membranes using improved enriched clay-polymer composites with surface hydrophilicity, water permeability, and antibacterial activity [53].

5.2 Drug Delivery and Other Biomedical Applications

In recent years, enriched clay/polymer composites have gained increasing attention in the biomedical field due to their excellent biocompatibility. Furthermore, the ability to mold into different shapes, including scaffolds, thin films, hydrogels, and fibers, high surface area to volume ratio, swellability, high retention, and excellent rheological properties, and the ability to blend with biopolymers have also extended their applications into a broad spectrum of biomedical applications [54].

Enriched nanoclay-polymer composites have been investigated for drug delivery applications because of their ability to interact with drug molecules, giving rise to favorable encapsulation, targeted delivery, and controlled release [55, 56]. More importantly, due to the multi-functionality of these enriched clay composites, they have been studied as anti-inflammatory, anticancer, and antimicrobial agents [57–59].

Most commonly used clay types in biomedical applications include bentonite, kaolinite, halloysite nanotubes (HNT), montmorillonite (MMT), attapulgite, sepiolite, and layered double hydroxides along with other polymer constituents [60–67]. These polymers, including cyclodextrin, poly(2-hydroxyethyl methacrylate), chitosan, carboxymethyl cellulose, gellan gum, and polyvinyl alcohol (PVA), have been employed to fabricate clay-polymer composites [68–73].

The clay-polymer composites generally improve the drug loading ability, and solubility of less water-soluble drugs and extend the drug release behavior, subsequently reducing the number of dosages applied, retaining the chemical activity of the drug while improving the efficiency of delivery and promoting the dose-specific targeted delivery to particular tissues and organs [74, 75]. For instance, anticancer clay-polymer composites can deliver anticancer drugs specifically to the tumor site [58].

Reddy et al. fabricated curcumin-encapsulated dual crosslinked sodium alginate and MMT polymeric composite beads for controlled drug delivery [76]. The addition of MMT has enhanced the bioavailability of curcumin, thereby triggering possible anticancer activity. Furthermore, the results indicated that incorporating multivalent ions such as Mg^{2+}, Ba^{2+}, and Al^{3+} ions into the alginate matrix via MMT improved the swelling properties and the curcumin release rate [76]. Figure 1 depicts the fabrication of a dual crosslinked sodium alginate/MMT drug carrier bead and the controlled release of curcumin drug [76].

In addition to drug delivery, clay/polymer composites have also been a choice for gene delivery, tissue engineering, wound healing, bio-imaging, and bio-sensing purposes. In gene delivery, clay minerals such as MMT, illite, kaolinite, and HNTs have been identified as potential vectors with a profound ability to bind DNA and protect them from degradation due to their polyelectrolyte nature [77]. However, to improve the degree of DNA binding, the use of various polymer molecules with

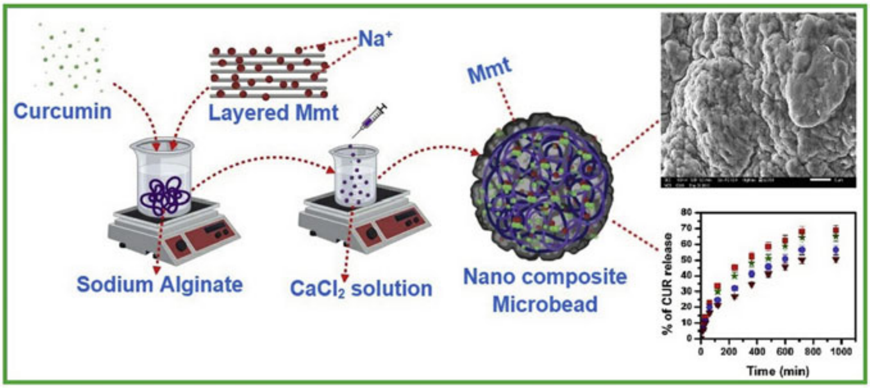


Fig. 1 Formation of the dual crosslinked sodium alginate-MMT polymeric bead performing as a controlled curcumin releasing drug carrier (Reprinted with the permission of the work of Reddy et al., 2021)

a positive charge, such as polyethylene imine (PEI), γ-aminopropyltriethoxysilane (APTES), and polyamidoamine along with the clay materials, have been considered [77–80].

For example, Long et al. employed polyethyleneimine (PEI), a branched polymer with an overall positive charge, to electrostatically interact with the negatively charged phosphate backbone of DNA and RNA molecules by increasing the interaction of genetic material with the polymer molecules. The authors reported an increase in the DNA binding efficiency upon the conjugation of PEI with the HNT [78].

The other common type of biomedical application of clay-polymer composites includes using them for tissue engineering purposes. The clay materials have been employed as scaffolding matrices to regenerate the damaged tissues and restore their function. Further, the content of the clay plays a crucial determinant in the elastic modulus of the scaffolds [81]. Combining the clay with biopolymers improves cell adhesion, proliferation, and differentiation, and enhances biocompatibility and the biodegradability of the tissue scaffolds. Moreover, combinations can act as filler materials giving rise to improved mechanical and physical properties of the tissue transplants [82]. Polysaccharides such as chitosan with clay materials like MMT have been utilized to prepare scaffolds from clay-polymer composites [83].

The emerging insights of 3D bioprinting technology and enriched clay-polymer composites have paved the way for designing groundbreaking, self-supporting hydrogel scaffolding matrices with improved mechanical and biological properties. Here, the clay-polymer composites act as bioinks, leading to the artificial organ construction and the generation of complex structures such as multilayered hollow tubes and cuboids and enhancing the colonization of preosteoblasts [84].

The work using laponite nanoclay to form 3D alginate-gelatin hydrogel provides an example of how the presence of nanoclay would improve the printability of the hydrogels enabling the formulation of complex detailed structures with less material spreading and pore closure [85].

Thermo-responsive and flexible scaffolding materials have also been fabricated using clay-polymer composites. For example, Shen and coworkers developed a thermo-responsive hydrogel composite using poly(N-isopropylacrylamide) and nanoclay, which exhibited high tensile strength and thermo-responsive swelling and deswelling characteristics [86].

In addition, the clay-polymer composites have also been useful in regenerating soft tissues in the liver, pancreas, and skin. The clay-polymer composite hydrogel prepared from gellan gum, HNT, and glycol showed reduced water uptake by 30–35% and increased viscosity making the composite hydrogel suitable for soft tissue applications [87]. One of the advanced applications of clay-polymer composites includes cell transplantation for neural tissue engineering due to their unique porosity, biocompatibility and biodegradability of the composite material [88].

Recent attention has also been paid to the development of clay-polymer composites as contrast agents for bio-imaging techniques, including magnetic resonance imaging (MRI), fluorescence imaging (FI), and photoacoustic imaging, mainly due to the excellent performance of the clay-polymer composites in terms of their penetration, high quantum yield, bio-distribution, and pharmacokinetics [89–91]. Furthermore, they have also been applied as potential sensor materials to detect harmful pathogens and different analytes linked to diseased conditions such as blood glucose and urea [92, 93]. Owing to their chemical versatility, physical stability, absorptivity, and the presence of mobile ions, their applicability in sensing applications is broader.[94] For instance, Zheng et al. developed a user-friendly, rapid point-of-care blood glucose detection unit with long-term stability using platinum nanoparticles bound with polyaniline MMT hybrid composite where the recovery of the glucose concentration varied from 95.1 to 103.2% [95].

Due to their profound antibacterial properties, clay-polymer composites have been applied for wound healing [96, 97]. For example, Sharma et al. prepared a clay-polymer composite using copper-modified MMT together with PVA for wound healing applications, outperforming the activity of the standard drugs [98]. Furthermore, the nanofiber synthesized from PVA, kaolinite, and Tragacanth Gum also exhibited improved mechanical and chemical stabilities and excellent wound healing properties [99]. Similarly, HNTs and polylactic acid (PLA) antibacterial membranes infused with gentamycin showed increased thermal and mechanical stability [46, 100]. Furthermore, these clay-polymer composites could also increase the antibacterial drug encapsulation and loading [46].

6 Conclusions

Enriched clay-polymer composites represent one of the most versatile materials to be employed in a diverse range of areas, including environmental, food and medical applications. Enriched clay-polymer composites display distinct characteristics due to their unique morphology, availability, and tailor-made composition, giving high mechanical ad physical strength, chemical stability, biodegradability, low cost, barrier properties, and cellular compatibility. This chapter comprehensively discussed utilizing clay-polymer composites in the industrial dye, pesticides, pharmaceuticals and phenolic contaminants and heavy metal removal, food packing, fire retardants, and medical fields, including antimicrobial agents, drug delivery, and other biomedical applications. One of the key challenges of intercalating clays into polymer matrices is the optimum amount of clay to be incorporated that is cellular compatible. One of the promising trends of enriched clay-polymer composites is their use in 3D printing and developing clay-polymeric inks. Moreover, enriched clay-polymer composites show potential to be applied as excellent advanced and smart materials for devising sensors, intelligent packaging materials, functional coatings, membranes, filters, theranostics, energy and electronics, and various other biomedical devices.

Acknowledgements The authors would like to thank the Research Council and the Department of Biosystems Technology at the University of Sri Jayewardenepura.

References

1. Rautureau, M., Gomes, C.D.S.F., Liewig, N., Katouzian-Safadi, M.: Clays and Health. Springer (2017)
2. Silva-Valenzuela, M.d.G., Chambi-Peralta, M.M., Sayeg, I.J., de Souza Carvalho, F.M., Wang, S.H., Valenzuela-Diaz, F.R.: Enrichment of clay from Vitoria da Conquista (Brazil) for applications in cosmetics. Appl. Clay Sci. 155, 111–119 (2018)
3. Bergaya, F., Lagaly G.: Purification of Natural Clays. In: Bergaya, F., Lagaly, G. (eds.) Developments in clay science, pp. 213–221. Elsevier (2013)
4. Barakan, S., Aghazadeh, V.: Separation and characterisation of montmorillonite from a low-grade natural bentonite: using a non-destructive method. Micro & Nano Letters **14**, 688–693 (2019)
5. Wang, G., Yu, D., Kelkar, A.D., Zhang, L.: Electrospun nanofiber: Emerging reinforcing filler in polymer matrix composite materials. Prog. Polym. Sci. **75**, 73–107 (2017)
6. Mukhopadhyay, R., Bhaduri, D., Sarkar, B., Rasmin, R., Hou, D., Khanam, R., Ok, Y.S.: Clay–polymer nanocomposites: Progress and challenges for use in sustainable water treatment. J. Hazard. Mater. **383**, 121125 (2020)
7. Zhang, T., Wang, W., Zhao, Y., Bai, H., Wen, T., Kang, S., Komarneni, S.: Removal of heavy metals and dyes by clay-based adsorbents: From natural clays to 1D and 2D nano-composites. Chem. Eng. J. **420**, 127574 (2021)
8. Sirajudheen, P., Karthikeyan, P., Basheer, M.C., Meenakshi, S.: Adsorptive removal of anionic azo dyes from effluent water using Zr(IV) encapsulated carboxymethyl cellulose-montmorillonite composite. Env. Chem. Ecotoxic. **2**, 73–82 (2020)
9. Sirajudheen, P., Karthikeyan, P., Vigneshwaran, S., Meenakshi, S.: Synthesis and characterization of La(III) supported carboxymethylcellulose-clay composite for toxic dyes removal: Evaluation of adsorption kinetics, isotherms and thermodynamics. Int. J. Bio. Macromol. **161**, 1117–1126 (2020)
10. Sirajudheen, P., Meenakshi, S.: Lanthanum (III) incorporated chitosan-montmorillonite composite as flexible material for adsorptive removal of azo dyes from water. Mater. Today Proceed. **27**, 318–326 (2020)
11. Khan, M.N., Chowdhury, M., Rahman, M.M.: Biobased amphoteric aerogel derived from amine-modified clay-enriched chitosan/alginate for adsorption of organic dyes and chromium (VI) ions from aqueous solution. Mater. Today Sustain. **13**, 100077 (2021)
12. Abukhadra, M.R., Shaban, M., Sayed, F., Saad, I.: Efficient photocatalytic removal of safarnin-O dye pollutants from water under sunlight using synthetic bentonite/polyaniline/Ni2O3 photocatalyst of enhanced properties. Env. Sci. Pollut. Res. **25**, 33264–33276 (2018)
13. Wang, W., Wang, J., Zhao, Y., Bai, H., Huang, M., Zhang, T., Song, S.: High-performance two-dimensional montmorillonite supported-poly(acrylamide-co-acrylic acid) hydrogel for dye removal. Env. Pollut. **257**, 113574 (2020)
14. Radoor, S., Karayil, J., Parameshwaranpillai, J., Siengchin, J.: Removal of anionic dye Congo red from aqueous environment using polyvinyl alcohol/sodium alginate/ZSM-5 zeolite membrane. Sci. Reports. **10**, 15452 (2020)
15. Mittal, H., Babu, R., Dabbawala, A.A., Stephen, S., Alhassan, S.M.: Zeolite-Y incorporated karaya gum hydrogel composites for highly effective removal of cationic dyes. Colloids Surf. A Physicochem. Eng. Asp. **586**, 124161 (2020)
16. Mittal, H., Al Alili, A., Alhassan, S.M.: High efficiency removal of methylene blue dye using κ-carrageenan-poly(acrylamide-co-methacrylic acid)/AQSOA-Z05 zeolite hydrogel composites. Cellulose **27**, 8269–8285 (2020)
17. Jawad, A.H., Abdulhameed, A.S.: Facile synthesis of crosslinked chitosan-tripolyphosphate/kaolin clay composite for decolourization and COD reduction of remazol brilliant blue R dye: Optimization by using response surface methodology. Colloids Surf. A Physicochem. Eng. Asp. **605**, 125329 (2020)

18. Narayanan, N., Gupta, S., Gajbhiye, V.T.: Decontamination of pesticide industrial effluent by adsorption–coagulation–flocculation process using biopolymer-nanoorganoclay composite. Int. J. Environ. Sci. Technol. **17**, 4775–4786 (2020)
19. Hernández-Hernández, K.A., Illescas, J., del Carmen Diaz-Nava, M., Martinez-Gallegos, S., Muro-Urista, C., Ortega-Aguilar, R.E., Rivera, E.: Preparation of nanocomposites for the removal of phenolic compounds from aqueous solutions. Appl. Clay Sci. **157**, 212–217 (2018)
20. Arya, V., Philip, L.: Adsorption of pharmaceuticals in water using Fe3O4 coated polymer clay composite. Micropor. Mesopor. Mater. **232**, 273–280 (2016)
21. Levy, L., A., Mishael, Y.G.: Enhanced gemfibrozil removal from treated wastewater by designed "loopy" clay-polycation sorbents: Effect of diclofenac and effluent organic matter. Appl. Clay Sci. 182, 105278 (2019)
22. Kumararaja, P., Manjaiah, K.M., Datta, S.C., Ahammed Shabeer, T.P., Sarkar, B.: Chitosan-g-poly(acrylic acid)-bentonite composite: a potential immobilizing agent of heavy metals in soil. Cellulose **25**, 3985–3999 (2018)
23. Moja, T.N., Bunekar, N., Mishra, S.B., Tsai, T.Y., Hwang, S.S., Mishra, A.k.: Melt processing of polypropylene-grafted-maleic anhydride/Chitosan polymer blend functionalized with montmorillonite for the removal of lead ions from aqueous solutions. Scientific Reports. 10, 217 (2020)
24. Chen, X., Cui, J., Xu, X., Sun, B., Zhang, L., Dong, W., Sun, D.: Bacterial cellulose/attapulgite magnetic composites as an efficient adsorbent for heavy metal ions and dye treatment. Carbohydr. Polym. **229**, 115512 (2020)
25. Moreno-Sader, K., Garcia-padilla, A., Realpe, A., Acevedo-Morantes, M., Soares, J.B.: Removal of Heavy Metal Water Pollutants (Co2+ and Ni2+) Using Polyacrylamide/Sodium Montmorillonite (PAM/Na-MMT) Nanocomposites. ACS Omega **4**, 10834–10844 (2019)
26. Kong, Y., Wang, L., Ge, Y., Su, H., Li, Z.: Lignin xanthate resin–bentonite clay composite as a highly effective and low-cost adsorbent for the removal of doxycycline hydrochloride antibiotic and mercury ions in water. J. Hazard. Mater. **368**, 33–41 (2019)
27. Pawar, R.R., Ingole, P.G., Lee, S.M.: Use of activated bentonite-alginate composite beads for efficient removal of toxic Cu2+ and Pb2+ ions from aquatic environment. Int. J. Bio. Macromol. **164**, 3145–3154 (2020)
28. Fahmy, H.M., Eldin, R.E.S., Serea, E.S.A., Gomaa, N.M., AboElmagd, G.M., Salem, S.A., Shalan, A.E.: Advances in nanotechnology and antibacterial properties of biodegradable food packaging materials. RSC Adv. **10**, 20467–20484 (2020)
29. Kamarudin, S.H., Rayung, M., Abu, F., Ahmad, S.B., Fadil, F., Karim, A.A., Abdullah, L.C.: A review on antimicrobial packaging from biodegradable polymer composites. Polymers **14**, 174 (2022)
30. Cheikh, D., Majdoub, H., Darder, M.: An overview of clay-polymer nanocomposites containing bioactive compounds for food packaging applications. Appl. Clay Sci. **216**, 106335 (2022)
31. Zeng, X., Zhong, B., Jia, Z., Zhang, Q., Chen, Y., Jia, D.: Halloysite nanotubes as nanocarriers for plant herbicide and its controlled release in biodegradable polymers composite film. Appl. Clay Sci. **171**, 20–28 (2019)
32. Yahiaoui, F., Benhacine, F., Ferfera-Harrar, H., Habi, A., Hadj-Hamou, A.S., Grohens, Y.: Development of antimicrobial PCL/nanoclay nanocomposite films with enhanced mechanical and water vapor barrier properties for packaging applications. Polym. Bull. **72**, 235–254 (2015)
33. Jafarzadeh, S., Alias, A.K., Ariffin, F., Mahmud, S., Najafi, A.: Preparation and characterization of bionanocomposite films reinforced with nano kaolin. J. food sci. technol. **53**, 1111–1119 (2016)
34. Neves, M.A., Hashemi, J., Yoshino, T., Uemura, K., Nakajima, M.: Development and characterization of chitosan-nanoclay composite films for enhanced gas barrier and mechanical properties. J. Food Sci. Nutr **2**, 1–7 (2016)

35. Moustafa, H., El-Sayed, S. M., & Youssef, A. M.: Synergistic impact of cumin essential oil on enhancing of UV-blocking and antibacterial activity of biodegradable poly (butylene adipate-co-terephthalate)/clay platelets nanocomposites. J. Thermoplast. Compos. Mater, 0892705721989771 (2021)
36. Kiliaris, P., Papaspyrides, C.D.: Polymer/layered silicate (clay) nanocomposites: an overview of flame retardancy. Prog. polym. sci. **35**, 902–958 (2010)
37. Sanchez-Olivares, G., Sanchez-Solis, A., Calderas, F., Medina-Torres, L., Manero, O., Di Blasio, A., Alongi, J.: Sodium montmorillonite effect on the morphology, thermal, flame retardant and mechanical properties of semi-finished leather. Appl. Clay Sci. **102**, 254–260 (2014)
38. Qin, H., Zhang, S., Zhao, C., Hu, G., Yang, M.: Flame retardant mechanism of polymer/clay nanocomposites based on polypropylene. Polym. **46**, 8386–8395 (2005)
39. Gilman, J. W., Kashiwagi, T., Lichtenhan, J. D.. Nanocomposites: a revolutionary new flame retardant approach. In: International sampe symposium and exhibition, pp. 1078–1089 (1997)
40. Qin, H., Su, Q., Zhang, S., Zhao, B., Yang, M.: Thermal stability and flammability of polyamide 66/montmorillonite nanocomposites. Polym. **44**, 7533–7538 (2003)
41. Qin, H., Zhang, S., Zhao, C., Feng, M., Yang, M., Shu, Z., Yang, S.: Thermal stability and flammability of polypropylene/montmorillonite composites. Polym. Degrad. Stab. **85**, 807–813 (2004)
42. Guo, Y., Chang, C.C., Halada, G., Cuiffo, M.A., Xue, Y., Zuo, X., Rafailovich, M.H.: Engineering flame retardant biodegradable polymer nanocomposites and their application in 3D printing. Polym. Degrad. Stab. **137**, 205–215 (2017)
43. Sabbagh, F., Kim, B.S.: Microneedles for transdermal drug delivery using clay-based composites. Expert Opin. Drug Deliv. **19**, 1099–1113 (2022)
44. Elbassyoni, S., Kamoun, E.A., Taha, T.H., Rashed, M.A., ElNozahi, F.A.: Effect of Egyptian attapulgite clay on the properties of PVA-HES–clay nanocomposite hydrogel membranes for wound dressing applications. Arab. J. Sci. Eng. **45**, 4737–4749 (2020)
45. Haque, M., Sartelli, M., McKimm, J., Bakar, M.A.: Health care-associated infections–an overview. Infect. Drug Resist. **11**, 2321 (2018)
46. Pierchala, M.K., Makaremi, M., Tan, H.L., Pushpamalar, J., Muniyandy, S., Solouk, A., Pasbakhsh, P.: Nanotubes in nanofibers: Antibacterial multilayered polylactic acid/halloysite/gentamicin membranes for bone regeneration application. Appl. Clay Sci. **160**, 95–105 (2018)
47. Garavand, F., Cacciotti, I., Vahedikia, N., Rehman, A., Tarhan, Ö., Akbari-Alavijeh, S., Jafari, S.M.: A comprehensive review on the nanocomposites loaded with chitosan nanoparticles for food packaging. Crit. Rev. Food Sci. Nut. **62**, 1383–1416 (2022)
48. Qu, B., Luo, Y.: Chitosan-based hydrogel beads: Preparations, modifications and applications in food and agriculture sectors—A review. Int. J. Bio. Macromol. **152**, 437–448 (2020)
49. Passaretti, M.G., Ninago, M.D., Villar, M.A., López, O.V.: Thermoplastic Starch and Mica Clay Composites as Biodegradable Mulching Films. J. Polym. Environ. **30**, 4394–4405 (2022)
50. Souza, R., Jha, A., Calabrese, S.: Quantifying the hydrological impact of soil mulching across rainfall regimes and mulching layer thickness. J. Hydrol. **607**, 127523 (2022)
51. Merino, D., Gutiérrez, T.J., Mansilla, A.Y., Casalongué, C.A., Alvarez, V.A.: Critical evaluation of starch-based antibacterial nanocomposites as agricultural mulch films: Study on their interactions with water and light. ACS Sustain. Chem. Eng. **6**, 15662–15672 (2018)
52. Asamoah, R.B., Yaya, A., Nbelayim, P., Annan, E., Onwona-Agyeman, B.: Development and characterization of clay-nanocomposites for water purification. Materials. **13**, 3793 (2020)
53. Ying, Y., Ying, W., Li, Q., Meng, D., Ren, G., Yan, R., Peng, X.: Recent advances of nanomaterial-based membrane for water purification. Appl. Mater. Today. **7**, 144–158 (2017)
54. Das, P., Manna, S., Behera, A. K., Shee, M., Basak, P., Sharma, A. K.: Current synthesis and characterization techniques for clay-based polymer nano-composites and its biomedical applications: A review. Environ. Res. 113534. (2022)
55. Voicu, A.I., Gârea, S.A., Vasile, E., Ghebaur, A., Iovu, H.: Hybrid Hosts Based on Sodium Alginate and Porous Clay Heterostructures for Drug Encapsulation. Polymers **13**, 2803 (2021)

56. Tipa, C., Cidade, M.T., Vieira, T., Silva, J.C., Soares, P.I., Borges, J.P.: A new long-term composite drug delivery system based on thermo-responsive hydrogel and nanoclay. Nanomater. **11**, 25 (2020)
57. Smiljanić, D., de Gennaro, B., Daković, A., Galzerano, B., Germinario, C., Izzo, F., Langella, A.: Removal of non-steroidal anti-inflammatory drugs from water by zeolite-rich composites: The interference of inorganic anions on the ibuprofen and naproxen adsorption. J. Environ. Manage. **286**, 112168 (2021)
58. Florian, P.E., Icriverzi, M., Ninciuleanu, C.M., Alexandrescu, E., Trica, B., Preda, S., Roseanu, A.: Salecan-clay based polymer nanocomposites for chemotherapeutic drug delivery systems; characterization and in vitro biocompatibility studies. Materials. **13**, 5389 (2020)
59. Stavitskaya, A., Batasheva, S., Vinokurov, V., Fakhrullina, G., Sangarov, V., Lvov, Y., Fakhrullin, R.: Antimicrobial applications of clay nanotube-based composites. Nanomater. **9**, 708 (2019)
60. Taaca, K.L.M., Dahonog, L.A., Olegario, E.M.: Cell viability and bacterial reduction activity of Ag-modified bentonite. Mater. Today: Proceed. **16**, 1782–1788 (2019)
61. Anand, R., Jeslin, J.: Synthesis of bentonite nanoclay and incorporation of cassia fistula leaf extract to form organobentonite: characterization and its biomedical applications. Synthesis. 11 (2018)
62. Awad, M.E., López-Galindo, A., Setti, M., El-Rahmany, M.M., Iborra, C.V.: Kaolinite in pharmaceutics and biomedicine. Int. J. Pharm. **533**, 34–48 (2017)
63. Fakhruddin, K., Hassan, R., Khan, M.U.A., Allisha, S.N., Abd Razak, S.I., Zreaqat, M.H., Hassan, A.: Halloysite nanotubes and halloysite-based composites for biomedical applications. Arab. J. Chem. **14**, 103294 (2021)
64. Chang, S.H., Hsieh, M.H.: Surface properties of chitosan/montmorillonite films for biomedical applications. Polym. Polym. Compos. **29**, 1442–1449 (2021)
65. Farid, E., Kamoun, E. A., Taha, T. H., El-Dissouky, A., Khalil, T. E.: PVA/CMC/attapulgite clay composite hydrogel membranes for biomedical applications: factors affecting hydrogel membranes crosslinking and bio-evaluation tests. J. Polym. Environ. 1–15 (2022)
66. Castro-Smirnov, F.A., Pietrement, O., Aranda, P., Le Cam, E., Ruiz-Hitzky, E., Lopez, B.S.: Biotechnological applications of the sepiolite interactions with bacteria: Bacterial transformation and DNA extraction. Appl. Clay Sci. **191**, 105613 (2020)
67. Yan, L., Gonca, S., Zhu, G., Zhang, W., Chen, X.: Layered double hydroxide nanostructures and nanocomposites for biomedical applications. J. Mater. Chem. B. **7**, 5583–5601 (2019)
68. Koohestani, F., Sadjadi, S., Heravi, M.: Composite of bentonite and cyclodextrin as an efficient catalyst for promoting chemical transformations in aqueous media. Sci. Rep. **11**, 1–10 (2021)
69. Șerban, M.V., Nazarie, S.R., Dinescu, S., Radu, I.C., Zaharia, C., Istrătoiu, E.A., Costache, M.: Silk proteinsenriched nanocomposite hydrogels based on modified MMT clay and poly (2-hydroxyethyl methacrylate-co-2-acrylamido-2-methylpropane Sulfonic Acid) display favorable properties for soft tissue engineering. Nanomater. **12**, 503 (2022)
70. Kouser, S., Sheik, S., Nagaraja, G.K., Prabhu, A., Prashantha, K., D'souza, J.N., Manasa, D.J.: Functionalization of halloysite nanotube with chitosan reinforced poly (vinyl alcohol) nanocomposites for potential biomedical applications. Int. J. Bio. Macromol. **165**, 1079–1092 (2020)
71. Palem, R.R., Rao, K.M., Shimoga, G., Saratale, R.G., Shinde, S.K., Ghodake, G.S., Lee, S.H.: Physicochemical characterization, drug release, and biocompatibility evaluation of carboxymethyl cellulose-based hydrogels reinforced with sepiolite nanoclay. Int. J. Bio. Macromol. **178**, 464–476 (2021)
72. Kouser, S., Sheik, S., Prabhu, A., Nagaraja, G.K., Prashantha, K., D'souza, J.N., Manasa, D.J.: Effects of reinforcement of sodium alginate functionalized halloysite clay nanotubes on thermo-mechanical properties and biocompatibility of poly (vinyl alcohol) nanocomposites. J. Mec. Behav. Biomed. Mater. **118**, 104441 (2021)
73. Pacelli, S., Paolicelli, P., Moretti, G., Petralito, S., Di Giacomo, S., Vitalone, A., Casadei, M.A.: Gellan gum methacrylate and laponite as an innovative nanocomposite hydrogel for biomedical applications. Europ. Polym. J. **77**, 114–123 (2016)

74. Liu, X., Lu, X., Su, Y., Kun, E., Zhang, F.: Clay-polymer nanocomposites prepared by reactive melt extrusion for sustained drug release. Pharmaceutics. **12**, 51 (2020)
75. Meirelles, L.M.A., Raffin, F.N.: Clay and polymer-based composites applied to drug release: A scientific and technological prospection. J. Pharm. Pharm. Sci. **20**, 115–134 (2017)
76. Reddy, O.S., Subha, M.C.S., Jithendra, T., Madhavi, C., Rao, K.C.: Curcumin encapsulated dual cross linked sodium alginate/montmorillonite polymeric composite beads for controlled drug delivery. J. Pharm. Anal. **11**, 191–199 (2021)
77. Batasheva, S., Kryuchkova, M., Fakhrullin, R., Cavallaro, G., Lazzara, G., Akhatova, F., Fakhrullin, R.: Facile fabrication of natural polyelectrolyte-nanoclay composites: Halloysite nanotubes, nucleotides and DNA study. Molecules **25**, 3557 (2020)
78. Long, Z., Zhang, J., Shen, Y., Zhou, C., Liu, M.: Polyethyleneimine grafted short halloysite nanotubes for gene delivery. Mater. Sci. Eng.: C. 81, 224–235 (2017)
79. Shi, Y.F., Tian, Z., Zhang, Y., Shen, H.B., Jia, N.Q.: Functionalized halloysite nanotube-based carrier for intracellular delivery of antisense oligonucleotides. Nanoscale Res. Lett. **6**, 1–7 (2011)
80. Liyanage, A.U., Ikhuoria, E.U., Adenuga, A.A., Remcho, V.T., Lerner, M.M.: Synthesis and characterization of low-generation polyamidoamine (PAMAM) dendrimer–sodium montmorillonite (Na-MMT) clay nanocomposites. Inorg. Chem. **52**, 4603–4610 (2013)
81. Mirakabad, F.S.T., Hosseinzadeh, S., Abbaszadeh, H.A., Zeighamian, V., Khoramgah, M.S., Ghanbarian, H., Kazemi, B.: Optimization of topography and surface properties of polyacrylonitrile-based electrospun scaffolds via nonoclay concentrations and its effect on osteogenic differentiation of human mesenchymal stem cells. Iran. J. Pharm. Res. **20**, 385 (2021)
82. Wong, L. W., Goh, C. B. S., Pasbakhsh, P., Tan, J. B. L.: Natural hollow clay nanotubes and their applications as polymer nanocomposites in tissue engineering. J. Sci.: Adv. Mater. Dev. 100431 (2022)
83. Barik, D., Kundu, K., Dash, M.: Montmorillonite stabilized chitosan-co-mucin hydrogel for tissue engineering applications. RSC Adv. **11**, 30329–30342 (2021)
84. Murugesan, S., Scheibel, T.: Copolymer/Clay nanocomposites for biomedical ppplications. Adv. Funct. Mater. **30**, 1908101 (2020)
85. Cai, F.F., Heid, S., Boccaccini, A.R.: Potential of Laponite® incorporated oxidized alginate–gelatin (ADA-GEL) composite hydrogels for extrusion-based 3D printing. J. Biomed. Mater. Res. B: Appl. Biomater. **109**, 1090–1104 (2021)
86. Shen, J., Li, N., Ye, M.: Preparation and characterization of dual-sensitive double network hydrogels with clay as a physical crosslinker. Appl. Clay Sci. **103**, 40–45 (2015)
87. Bonifacio, M.A., Gentile, P., Ferreira, A.M., Cometa, S., De Giglio, E.: Insight into halloysite nanotubes-loaded gellan gum hydrogels for soft tissue engineering applications. Carbohydrate Polym. **163**, 280–291 (2017)
88. Ahmadi, S., Shafiei, S.S., Sabouni, F.: Electrospun nanofibrous scaffolds of polycaprolactone/gelatin reinforced with layered double hydroxide nanoclay for nerve tissue engineering applications. ACS Omega **7**, 28351–28360 (2022)
89. Zhao, M., Tang, Z., Zhang, J., Fu, G., Xu, W., Wu, Q., Pu, L.: Preparation and MRI performance of a composite contrast agent based on palygorskite pores and channels binding effect to prolong the residence time of water molecules on gadolinium ions. RSC Adv. **12**, 7328–7334 (2022)
90. Zhong, J., Li, Z., Guan, W., Lu, C.: Cation– π interaction triggered-fluorescence of clay fillers in polymer composites for quantification of three-dimensional macrodispersion. Anal. Chem. **89**, 12472–12479 (2017)
91. Liu, R., Xu, F., Wang, L., Liu, M., Cao, X., Shi, X., Guo, R.: Polydopamine-coated laponite nanoplatforms for photoacoustic imaging-guided chemo-phototherapy of breast cancer. Nanomater. **11**, 394 (2021)
92. Moulahoum, H., Ghorbanizamani, F., Guler Celik, E., Timur, S.: Nano-scaled materials and polymer integration in biosensing tools. Biosensors **12**, 301 (2022)

93. Pavón, E., Martín-Rodríguez, R., Perdigón, A. C., Alba, M. D.: New trends in Nanoclay-modified sensors. Inorganics. **9**(43), (2021)
94. Lopes, A.C., Martins, P., Lanceros-Mendez, S.: Aluminosilicate and aluminosilicate based polymer composites: present status, applications and future trends. Prog. Surf. Sci. **89**, 239–277 (2014)
95. Zheng, H., Liu, M., Yan, Z., Chen, J.: Highly selective and stable glucose biosensor based on incorporation of platinum nanoparticles into polyaniline-montmorillonite hybrid composites. Microchem. J. **152**, 104266 (2020)
96. García-Villén, F., Faccendini, A., Miele, D., Ruggeri, M., Sánchez-Espejo, R., Borrego-Sánchez, A., Sandri, G.: Wound healing activity of nanoclay/spring water hydrogels. Pharmaceutics. **12**, 467 (2020)
97. Zeaiean Firouzabadi, P., Ghanbari, H., Mahmoudi, N., Haramshahi, S. M. A., Javadpour, J.: Synthesis of nanobentonite–poly (vinyl alcohol)–bacterial cellulose nanocomposite by electrospinning for wound healing applications. Physic. Status Solid. (a). 217, 1900536 (2020)
98. Sharma, B., Jain, P., Purwar, R.: Preparation and characterization of poly (vinyl alcohol)/ modified clay electrospun nanocomposite nanofibrous mats for microbial protection. J. Text. Inst. **110**, 1624–1634 (2019)
99. Heydary, H.A., Karamian, E., Poorazizi, E., Khandan, A., Heydaripour, J.: A novel nanofiber of Iranian gum tragacanth-polyvinyl alcohol/nanoclay composite for wound healing applications. Proced. Mater. Sci. **11**, 176–182 (2015)
100. Saadat, S., Pandey, G., Tharmavaram, M., Braganza, V., Rawtani, D.: Nano-interfacial decoration of Halloysite Nanotubes for the development of antimicrobial nanocomposites. Ad. Coll. Interf. Sci. **275**, 102063 (2020)

Clay–Polymer Adsorbents for the Treatment of Industrial Effluents

Hansini Abeysinghe and Thusitha N. B. Etampawala

Abstract The development of efficient industrial effluent treatment methods is one of the significant challenges the world faces with continuous industrialization and urbanization. Though various effluent treatment methods have been developed, adsorption is more favoured due to its effectiveness, efficiency, and ease of operation. Among various adsorbents, growing attention has been placed on clay–polymer composites to treat industrial effluents mainly because of their easy manipulation and flexible nature. In this respect, this chapter describes various types of clay–polymer adsorbents designed to treat industrial effluents such as dyes, heavy metals, plasticizers, and other organic small molecules, with their adsorption mechanisms and factors affecting the adsorption efficiency. Furthermore, this article explores a concise overview of the primary classifications of clay-polymer composites, namely exfoliated, intercalated, and phase-separated, along with a thorough examination of their respective fabrication methods. Additionally, the article explores various techniques employed for characterization purposes. In the end, the challenges and future perspectives regarding the use of clay–polymer adsorbents to treat industrial effluents are addressed.

Keywords Clay minerals · Polymer composites · Wastewater treatments · Industrial effluents

---

H. Abeysinghe
Department of Polymer Science, School of Polymer Science and Polymer Engineering, The University of Akron, Akron, OH 44325, USA

T. N. B. Etampawala (✉)
Department of Polymer Science, Faculty of Applied Sciences, University of Sri Jayewardenepura, Nugegoda 10500, Sri Lanka
e-mail: tetampa@sjp.ac.lk

Center for Nanocomposite Research, Faculty of Applied Sciences, University of Sri Jayewardenepura, Nugegoda 10500, Sri Lanka

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_14

1 Introduction

Developing various efficient and effective wastewater treatment technologies has become a highly researched area for the past several decades with global attention on finding solutions for water scarcity. With the continuous growth of global population and demands for purified drinking water, worldwide water usage has increased by around 1% each year since the 1980s. It is estimated to have a 20–30% increase in water usage by 2030 due to the high domestic and industrial demand with respect to the water usage in year 2019 (UNWater, 2019). However, the continuous use of freshwater without proper wastewater treatment plans has led to various complications, including the lack of access to safe water, pollution of groundwater sources, and the potential to cause various health hazards [48–50].

Moreover, it has been identified that reusing the treated-waste water might be a possible solution for handling the industrial and agricultural water demand. As reported in 2022, 32 and 19.3% of treated wastewater have been used for agricultural and industrial purposes [49] . That is why much attention has been placed over the past several years on developing efficient and effective wastewater treatment technologies. As of 2020, based on the statistical studies conducted by [22], it was estimated that 48% of the globally generated wastewater was released untreated into the environment, which was previously assumed to be 80% by the scientific community. Nevertheless, the lack of worldwide real-time data related to wastewater generation, effectiveness and efficiency of already in-use water treatment technologies, and the reusability of treated wastewater have made it difficult to evaluate the situation at hand [22, 49] . However, with a broad spectrum of wastewater generating sources, for ease of management and target treatment, wastewater has been categorized into four well-defined types: stormwater run-off, domestic, agricultural, and industrial [2]. Since this chapter is about using clay/polymer adsorbents to treat industrial effluents, some details related to industrial water usage will be discussed.

There is a high demand for water in the industrial sector since it has been used for various purposes including but not limited to dilution, washing, cooling equipment, and steam generation. According to AQUASTAT Database, the worldwide industrial water withdrawal percentage related to the total freshwater withdrawal is about 19% [16]. However, not following a proper wastewater treatment plan before releasing the used water into the environment has resulted in polluting water sources causing danger to the surrounding ecological systems. The nature and type of industrial effluents (dissolved and suspended substances present in the industrial wastewater) would vary based on the industry or the factory they get discharged [2]. Dyes (from the textile, paint, and dye manufacturing industries), heavy metals (from textile, pharmaceutical, paper, and chemical industries), and organic pollutants (from oil refining, textile, and drug manufacturing industries) are some primary industrial effluents that are found in industrial wastewater [2]. These effluents' toxicity and hazardous nature have shown the potential to cause cancer, neurological disorders, immunological problems, and many other health problems [41, 44]. Therefore, removing these pollutants and improving the water quality are necessary before releasing wastewater into the environment or reusing them for industrial applications.

Over the years, different technologies have been introduced and used to remove industrial effluents in wastewater. Some developed techniques include coagulation, chemical precipitation, ion exchange, electrolysis, photocatalysis, electrodialysis, and reverse osmosis [2, 6, 14]. Even though these techniques seem promising wastewater treatment methods, their high cost, not being developed up to industrial usage, formation of sludge leading to secondary treatments, and generation of secondary pollutants have limited the usage of these techniques in the real world [6, 7]. However, based on the current reports on water treatment methods, high-income countries seem to make more use of these techniques compared to low-income countries. On average, high-income countries only release 30% of untreated wastewater into the environment. In contrast, upper-middle-income, low-middle-income, and low-income countries release about 62, 72, and 92% of untreated wastewater, respectively UNESCO [49] . It is evident that even though the advanced technological wastewater treatment technologies are more effective and efficient, low-income countries have difficulties accessing them.

Comparatively, adsorption [7, 19, 39] is considered one of the most cost-effective, efficient, and suitable water purification technology for developing countries. As a result, more attention has been placed on developing various adsorbents using natural or/and synthetic materials because this technique is more cost-effective and produces fewer secondary pollutants, unlike other advanced techniques. However, selecting suitable adsorbents would depend on several factors: adsorption capacity and selectivity towards the targeted contaminant, cost/efficiency ratio, performance in the presence of different types and concentrations of target contaminant, availability, and ability to regenerate [6, 39]. Some adsorbents for wastewater treatment include activated carbon, agricultural waste, biochar, polymer resins, industrial waste, natural clay minerals, modified clays, and silica beads [27, 45, 17].

Out of these adsorbents, naturally occurring clay minerals [36, 47, 53] seem to have taken much attention in the wastewater treatment area because of their economic benefits of being highly abundant and cheap compared to other adsorbent materials. However, their low adsorption capacity towards organic contaminants, having low surface area resulting in low removal efficiency, the difficulty of recovering them from an aqueous solution after treatment, and complications in regenerating them have limited the use of clay minerals in real-world wastewater treatment applications. In contrast, polymer [23, 24, 51] resins show significant performance at water purification. High surface area, ability to adsorb a broad range of contaminants, and ease of modifying and regeneration without losing properties make them more desirable than other available adsorbents. Regardless of polymers' efficiency and effective adsorbent properties, their dependence on pH, low wettability, and performance that depends on the type, surface area, and porosity of the polymer caused some limitations on their usage in wastewater treatments. Moreover, their high cost prevents them from being used by developing countries. However, researchers have been working on developing clay/polymer adsorbents by combining their advantageous properties that show the potential to overcome their respective limitations over the past years to develop cost-effective, more efficient, and effective adsorbents [36, 39].

This chapter describes various clay/polymer adsorbents recently developed to treat industrial effluents (dyes, heavy metals, and organic pollutants) along with their adsorption mechanisms and factors affecting the adsorption efficiency. Moreover, this chapter provides brief information about the three main types of clay/polymer adsorbents (intercalated, phase-separated, and exfoliated), fabrication methods, and characterization techniques. In addition, the future perspective and challenges related to developing and using clay/polymer adsorbents for treating industrial effluents are addressed towards the end of this chapter.

2 Clay/Polymer Adsorbents

Clay minerals [6, 7, 30] are complex silicates of various ions (aluminium, magnesium, and iron), which consist of two basic crystalline units of silicon-oxygen tetrahedrons and aluminium or magnesium octahedrons. The tetrahedron crystal units (four oxygen atoms surrounding a Si^{4+}) form tetrahedral sheets. In contrast, the octahedral units (Mg^{2+} or $Al3^{3+}$ons surrounded by hydroxyl groups) form octahedral units. The plate-like stratified structures are formed by the combination of these octahedral and tetrahedral combinations, which are bound by the shared oxygen atoms. These structures are in general called phyllosilicates. These phyllosilicates are the basic structural units of aluminosilicate layers of clay minerals. The isomorphous substitution of ions within the clay mineral structure, where cations like Si^{4+}, Al^{3+}, and Mg^{2+} could be replaced by similar-sized ones, allows clay minerals to have both positive and negative charges.

Polymers are macromolecules consisting of covalently bonded repeating units. These can be either natural or synthetic polymers based on their sources. Moreover, polymers can have various microstructures such as linear, branched, crosslinked, or complex architecture-like dendrimers. Multiple polymers have taken significant attention in many research fields [10, 37] due to their ease of manipulation and flexibility in adjusting their properties per the target application: high mechanical strength, high chemical stability, high surface area, surface functionalization to tune to absorptivity, better selectivity towards target molecules, almost no loss of properties after regeneration, improved processability, and ease of recovery after using for water treatments.

More efficient and effective polymeric adsorbents have been developed [10, 21, 46], by making composites with non-polymeric dispersed phases such as activated carbon, carbon nanotube, and clay minerals to have a combination of properties of both materials. Clay/polymer adsorbents are composite materials developed by combining polymer and clay minerals to achieve beneficial properties to overcome some limitations of new materials. For instance, polymeric material by itself is very expensive, and they have low wettability and low absorptivity towards organic contaminants and low adsorption efficiency. In contrast to that, most of the clay minerals have a high surface area, different surface functionalizations, high wettability, and ability to adsorb most of the organic contaminants. Consequently combining both clay and polymeric resin can create new materials that gain significant attention as adsorbents for treating industrial effluents and have become more desirable and cost-effective over other the different adsorbents currently in use. Moreover, these clay/polymer adsorbents seem to be a potential solution for wastewater treatment in low-income countries owing to their low manufacturing cost.

2.1 Types of Clay/Polymer Adsorbents

Based on the modification methods, clay/polymer adsorbents can be either micro- or nano-scale composites. They can be classified into three main well-defined categories [36, 39]: phase-separated composites, intercalated composites, and exfoliated composites as shown in Fig. 1.

2.1.1 Phase-Separated Clay/polymer Composites

Phase-separated composites are micro-composites, where polymer chains surround clay platelets without penetrating the clay platelets. The clay platelets are in micrometre length scales and their pristine gallery spaces are not disturbed. The lack of penetration of clay platelets by polymer chains may result in micron-sized agglomerations within the polymer matrix. Therefore, one can consider that agglomerated clay platelets as a separate phase (dispersed phase) in a continuous polymer matrix.

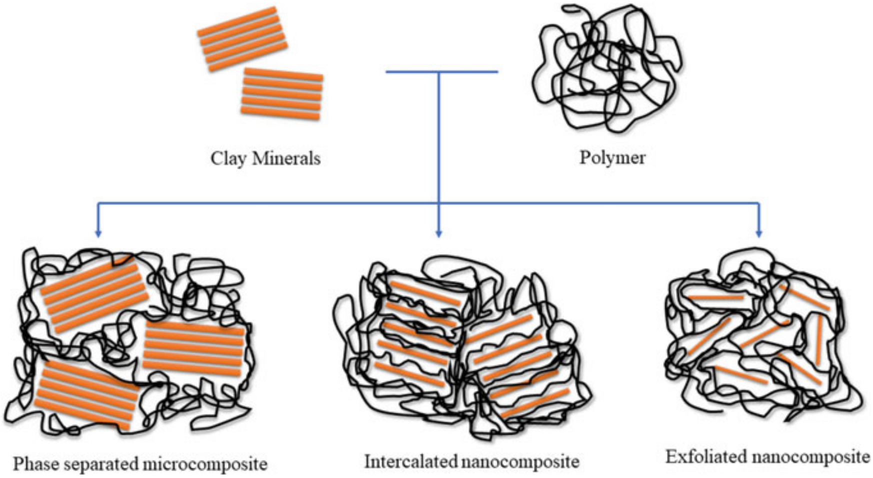


Fig. 1 Three main types of clay/polymer nanocomposites

These composites generally show typical characteristics of conventional dispersion strengthen particle reinforced composites.

2.1.2 Intercalated Clay/polymer Composites

Intercalate polymer composites are formed when the insertion of some polymer chains or segments of polymer chains inside the stratified layers. Consequently, the interlayer distance of clay particles increases but is not disengaged. This is an in-between stage of phase-separated and exfoliated composites.

2.1.3 Exfoliated Clay/polymer Nanocomposites

Further insertion of polymer chains to the interlayer gallery spaces may weaken the interlayer interactions. As a result, the platelets delaminate from each other. If the compatibility of the clay and the polymer is good the delaminated clay platelets disperse throughout the polymer matrix. Compared to the other two types of clay/polymer composites, exfoliated composites have a high surface area and can be considered a nanocomposite since the thickness of individual platelet structures are in nanometre length scales.

The exfoliated clay/polymer nanocomposites have better properties such as good barrier properties, thermal and mechanical stability, and many other properties than the micro-composites. Therefore, clay/polymer nanocomposites have been widely investigated as efficient and effective adsorbents for the removal of contaminants present in water [28, 7].

2.2 Fabrication Methods of Clay/polymer Nanocomposites

The fabrication method is crucial in developing high-efficiency clay/polymer adsorbents. Therefore, it is essential to fabricate a nanocomposite with homogeneously distributed clay platelets within the continuous polymer matrix. The fabrication method, choice of the clay mineral type, and their characteristics play a huge role in the distribution of the clay particles in the polymer matrix. To get better properties, it is essential to break down the large clay aggregates into small clay particles so that they can entangle with a matrix material. Otherwise weak inter-particle interaction may act as initiation points of damage.

Most clay minerals are hydrophilic; therefore, they are not compatible with hydrophobic polymers such as polystyrene and polyethene, but they are compatible with hydrophilic polymers polyvinyl alcohol and polymethyl methacrylate. Incompatibility between the polymer matrix and the dispersed clay minerals would cause agglomerations or phase separation instead of the desired dispersion. Therefore, it is crucial to modify the surface of clay platelets to be compatible with hydrophobic polymers before mixing to obtain homogeneous dispersion throughout the composite. Developing these organoclays is the primary step in producing clay/polymer nanocomposites [36]. The surface modification of clay minerals using organic molecules could be done in several ways:

I. Ion exchange processes using cationic surfactants (ex: alkyl phosphonium-based cationic species or coupling agents, quaternary alkylammonium salt)
II. Addition of coupling agent (ex: silane)
III. Ionic modification (directly reaction with ionic liquid or ionic surfactant)
IV. Covalent modification
V. Dual modifications (covalent and ionic modifications)
VI. Grafting polymers directly onto the clay platelet
VII. Modifications using non-ionic surfactants.

When considering the fabrication methods of clay/polymer nanocomposites [11, 36, 7], three main fabrication methods have been widely used: in situ polymerization, solution polymerization, and melt bending polymerization.

2.2.1 In Situ Polymerization

In the in situ polymerization, clay nanoparticles are first dispersed in a monomer solution. Here, the nanoplatelets get swelled with a monomer solution, where monomers get incorporated into the interlayers of clay platelets since they are significantly smaller than polymer chains. At a later stage by giving desired polymerization condition, these monomers will polymerize. After that, the formed polymer blend will be added to a bulk polymer matrix as a reinforcing material to obtain a uniform dispersion of clay nanoparticles within the continuous polymer matrix. Since this technique works with monomers and can use any appropriate polymerization technique, it is easy to develop clay/polymer nanocomposites compared to the other two techniques of making polymer/clay composites.

2.2.2 Solution Blending Polymerization

Two liquid phases are involved in solution blending: a solution with nanoparticles dispersed in a solvent and a solution of a polymer in the same solvent. Here, the solvent is in general referred to as co-solvent. These two solutions are mixed and then homogenized to have a uniform dispersion throughout the mixture. During this process, the clay platelets are swelled with solvent molecules and polymer chains or part of polymer chains are inserted into the interlayers between the clay sheets. If prepolymers are used with the solution, appropriate polymerizations must be performed to complete the polymerization of those prepolymers. This process would result in a highly dispersed exfoliated nanocomposite. Finally, the solvent molecules need to evaporate.

2.2.3 Melt Blending Polymerization

In melt blending polymerization, the clay nanoplatelets are directly mixed with a molten polymer matrix. In general, a polymer is melted using an extruder or internal mixer and then the desired amount of clay particles are added. This process can be of two types:

I. Immobile melt blending or melt annealing polymerization

Here, the melt blending polymerization is carried out under vacuum conditions at temperatures of about 50 °C higher than the transition temperatures without mixing.

II. Active melt blending polymerization

Here, the polymer melting is done during the melt mixing in an inert environment. Therefore, these composites are formed because of the enthalpic driving forces, and the intermolecular interactions occur during the mixing process.

2.3 Characterization Techniques for Clay/polymer Nanocomposites

After the nanocomposite fabrication, the next most important step is to analyse the structural, physical, mechanical, and chemical properties. Since the adsorbent properties of the clay/polymer adsorbents mostly rely on the morphological characteristics of the composites, it is crucial to analyse them. Various characterization techniques can also be used to observe the performance and mechanism of these developed adsorbents. Therefore, this section briefly describes essential characterization techniques for the analysis of clay/polymer nanocomposites [11, 20].

2.3.1 X-ray Diffraction (XRD)

XRD is a rapid analytical technique used to study the structural and crystalline characteristics of clay/polymer nanocomposites. This technique provides information related to the unit cell, phase, crystal arrangement, and spacing between the atomic layers of the analysing material. The interlayer distances of the clay minerals may change during the fabrication process of the composite. In intercalated clays, the interlayer distance increases with respect to its pristine form while in exfoliated clays no interlayer gaps can be identified since all the layers are disintegrated. Most of the clays have interlayer distances of sub-nm to nm length scales. These distances can easily be characterized by D-ray diffractograms. Pristine clay samples will give a sharp peak at low scattering angles, which will further move towards low scattering angles and become broader with intercalation. The stratified arrangement is no longer available after exfoliation, and thus, no repeating distances exist. Thus, the XRD peak appeared for the repeating distances of intercalated and pristine clay minerals that will disappear after exfoliation.

2.3.2 Transmission Electron Microscopy (TEM)

TEM can be used to analyse the internal structure of the clay/polymer nanocomposite. Therefore, this technique can be used to study the dispersion of clay nanoplatelets and other molecules within the polymer matrix. Moreover, with this visual inspection, various information such as exact morphological structure, distribution of clay platelets, the type of clay/polymer composite, and the distance between interlayers of clay platelets before and after modification can be identified. In addition, the TEM images taken before and after the adsorption could be used to study the adsorption behaviour of these developed nanocomposites. However, the drawback of this technique is the involvement of sophisticated sample preparation because TEM needs very thin composite specimens.

2.3.3 Scanning Electron Microscopy (SEM)

The SEM technique is mainly used to analyse the surface of a material. Therefore, the surface morphology of the developed nanocomposite could be studied using this technique. The cross-section of the composites can also be studied by SEM. However, it involves additional sample preparation steps. Cryo-fracturing or microtome can be used to break the sample without denaturing the cross-section. Then, the fractured cross-section can be studied and get the morphological details of the core of the material. This technique has been used to study the surfaces of recoverable and recyclable adsorbents as well.

2.3.4 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy is a useful analytical technique to study the composite's molecular structure. This analytical technique can identify the functional groups present in the polymer matrix of the nanocomposites based on the bands that occurred or disappeared at specific vibration frequencies when incident IR radiation interacts with the analysing compound. This technique is especially useful to characterize the modifications done to the clay particles. Especially the chemical bonds formed and/or disappeared between modified clay and polymer matrices.

2.3.5 Nuclear Magnetic Resonance (NMR) Spectroscopy

The NMR technique can be considered one of the most effective and powerful analytical techniques available to study the physiochemical properties of a material. NMR spectroscopy can be of different types (ex: 13C, 1H1, 15N). Therefore, the chemical structure of the developed clay/polymer nanocomposite can be determined using different types of NMR spectroscopies. Moreover, this will provide information related to the intermolecular interactions, molecular arrangements, and chemical bonds present within the nanocomposite. Further, the spin relaxation of matrix polymer in the presence and absence of clay particles can be studied by NMR techniques which gives some idea about the interaction between the polymer matrix and the clay dispersed phase.

2.3.6 Brunauer–Emmet–Teller (BET) Method

BET or gas (N_2, He, or Ar) adsorption–desorption analysis can be used to get specific surface area, average pore size, and pore size distribution of the clay minerals and the developed clay/polymer nanocomposite. This information can be correlated with the adsorption efficiency of the developed adsorbent.

2.3.7 Dynamic Mechanical Analysis (DMA)

DMA is an analytical tool used to identify the viscoelastic properties of a material. Therefore, the loss and storage modulus and the damping factor of the polymer used in the developed nanocomposite can be determined using this technique. This is a good technique to study the mechanical stability and transitional properties of matrix polymer after combining with the clay minerals.

2.3.8 Thermogravimetric Analysis (TGA)

TGA is an analytical tool used to study a compound's thermal stability. Developing an adsorbent that can withstand the harsh conditions of the potentially applicable environment is crucial. In general, thermal stability of the matrix martial is altered after the incorporation of clay minerals. Therefore, this technique can be used to study that effect.

2.3.9 Differential Scanning Calorimetry (DSC)

DSC analysis can be used to study the glass transition, crystallization, melting and curing behaviours of the polymer matrix, and the developed clay/polymer nanocomposite. This is a very good technique to identify whether clay particles reinforce the polymer matrix or not. The change of glass transition temperatures of the matrix polymer would be a key parameter to be considered.

3 Adsorption of Clay/Polymer Composites

As mentioned in the introduction, among advanced wastewater treatment technologies, significant attention has been placed on adsorption materials and methods due to their simplicity, low cost, and ease of operation. However, during this process [36], contaminants (adsorbate) present in the wastewater form interactions with the clay/polymer composite (adsorbent) surface, such that they can be removed from the wastewater. Moreover, an efficient and effective adsorbent must be able to remove the adsorbed contaminant from its surface and reuse it for water purification without significant loss of adsorption capacity. Therefore, it is essential to understand the adsorption mechanisms and the factors affecting the adsorption performance to develop a more efficient and effective adsorbent.

3.1 Adsorption Mechanisms

The adsorption mechanisms of contaminants in wastewater into clay/polymer composite [10, 53] can mainly be of two types: chemisorption and physisorption.

3.1.1 Chemisorption

Here, the adsorption occurs through the chemical bond formation between the adsorbate and the adsorbent. The chemical bond formation could be an electrostatic interaction, ionic exchange, reduction/oxidation, or complex formation (chelation) between the adsorbate and the adsorbent. In addition, the adsorption mechanism related to the developed adsorbent might depend on the presence of/ incorporated functional groups onto the surface of the adsorbent. Therefore, the complexity of the adsorption mechanism may depend on the nature of the adsorbent. However, kinetic studies have shown that the adsorption efficiency depends on the adsorbate and the adsorbent concentration.

3.1.2 Physisorption

Here, unlike the previously mentioned mechanism, the adsorbates only form weak physical interactions with the surface of the adsorbent, such as Van der Waals interactions. Since contaminants (adsorbate) only form weak interactions with the surface of the adsorbent (composite), their adsorption and desorption rates are comparatively high. As a result, this mechanism is reversible to a certain extent. Moreover, the formation of these weak interactions could be controlled via the temperature and pressure of the medium. Based on the kinetic studies, their adsorption efficiency depends only on the concentration and surface area of the adsorbent.

Moreover, studying the isothermal, kinetic, and thermodynamic aspects of the developed adsorbent would give more insight into their adsorption mechanisms.

3.2 Factors Affecting the Adsorption

Several crucial factors affect the performance of the clay/polymer adsorbents. Therefore, it is vital to study these factors and identify the optimal conditions for the developed nanocomposite. In this section, some such factors [6, 17, 36] are briefly discussed.

3.2.1 Surface Area

The surface area of the adsorbent is one of the most crucial factors determining an adsorbent's efficiency and effectiveness. It is vital to have a high surface area on the adsorbent such that the adsorbent can meet more contaminants in the wastewater. Careful fabrication is essential to get a composite with a homogeneous distribution of clay in a polymer matrix with unblocked adsorption sites. Exfoliated clay/polymer nanocomposites make more efficient and effective adsorbents than the other two types of clay/polymer composites.

3.2.2 Compatibility

The other crucial factor that needs to be considered is the compatibility between the adsorbate and the adsorbent. Since adsorption is solely dependent on the interactions between them, it is vital to develop the adsorbent in such a way that it can form interactions with the contaminants. Moreover, developing an effective adsorbent for a broad range of contaminants would be economically beneficial. Especially with the development of adsorbents by combining hydrophobic polymers and hydrophilic clay minerals show the potential at removing hydrophilic (heavy metals, dyes) and hydrophobic contaminants (organic pollutants, oil spill) from the wastewater. That is why clay/polymer adsorbents have taken significant attention in wastewater treatment.

3.2.3 PH Value

pH value of the solution may affect the surface charge present on the adsorbent and adsorbate which might affect the interactions formed between them. Moreover, the adsorption and desorption of contaminants from the adsorbent surface might be able to do just by controlling the pH value of the solution. Therefore, it is crucial to study the effect of the pH on the adsorption capacity of the clay/polymer composites.

3.2.4 Contact Time

The contact time between the adsorbent and the contaminants present in the water could significantly affect the adsorption efficiency. Therefore, it is crucial to identify the optimal contact time, such that the highest adsorption efficiency and capacity can be achieved.

3.2.5 Adsorbent Dosage

Adsorbent dosage (amount of adsorbent in a unit amount of matrix polymer) is another factor that needs to be considered when identifying the optimal conditions for the performance of the developed adsorbent. It is a known fact that more adsorbents would be adsorbates onto the surface. Nevertheless, identifying the minimum amount of adsorbate needed for the highest adsorption is more economically favourable.

3.2.6 Co-Existing Ions

Another vital factor that needs to be considered is studying the effect of co-existing ions or compounds in wastewater on the adsorbent's performance. These ions or compounds might affect the interactions between the adsorbent and the contaminant, lowering the adsorption efficiency.

4 Clay/Polymer Adsorbent for the Treatment of Industrial Effluents

This section discusses clay/polymer adsorbents developed for treating industrial effluents (dyes, heavy metals, and organic pollutants) over the past two years.

4.1 The Removal of Dyes

Dyes [13] are colourants widely used in many industries such as textile, paper-making, rubber, dyeing, and printing industries. They are generally organic molecules having characteristic chromophoric (–NH2,–NHR, –NR2 –OH, –COOH) and auxochromic (–NO, –NO2, –N2) groups [27]. These can be cationic, anionic, non-ionic, or amphipathic based on their chemical structures. However, over the years, wastewater containing these hazardous dye chemicals have been released into the environment without proper treatment [8]. The textile industry is one of the world's most widely spread industries,its contribution to water pollution seems considerably higher than other industries [33]. Therefore, nowadays, dyes are considered to be one of the major industrial contaminants found in wastewater. Most of them are hydrophilic, and dissolved in water makes them challenging to remove. However, it is vital to develop water purification methods that could remove these dyes at least to minimize the hazardous health impact on humans, animals, and plants [33]. Over the past two years, different kinds of research studies have been done on developing clay/polymer adsorbents for the removal of various dyes present in wastewater. Some of those research studies have been summarized in Table 1.

As discussed earlier, the clay/polymer composites seem to perform better as adsorbents than those used alone, as predicted. [23] have reported the synthesis of polyaniline/montmorillonite clay (PANI/MMT) adsorbent to remove Acid Green 25 dye from wastewater. According to this study, PANI/MMT polymer/clay composite had shown better dye absorbance than when PANI alone was used as the adsorbent. Based on the adsorption capacity calculated using the Langmuir isotherm, PANI/MMT showed an adsorption capacity of 51.02 mg/g, whereas PANI only showed about 34.14 mg/g adsorption.

Moreover, the research study by [3] shows the enhanced dye absorptivity of ethyl cellulose polymer with the incorporation of clay particles. In this study, the adsorption performance of ethyl cellulose/bentonite composite for the removal of methylene blue dye was studied. According to the Langmuir model, the maximum adsorption capacity of the monolayer for the composite is four times that of the polymer alone.

4.2 The Removal of Heavy Metals

A group of metals or metalloids having 63.5–200.6 gmol-1 molecular weight with a density greater than 5 gcm-3 are considered to be heavy metals [12]. Heavy metals are another abundant pollutant found in industrial wastewater. Routes that introduce heavy metals into fresh water could be the discharge of industrial waste, municipal waste, sewage, and agricultural wastewater. Moreover, with the industrialization and emergence of various technologies, the uncontrollable release of pollutants containing heavy metals has been happening continuously over the years. The contribution of iron and steel industry, electroplating industry, mining industry, organic and

Table 1 Clay/polymer adsorbents for the removal of dye molecules from the wastewater

Polymer	Clay mineral	Dye	Removal efficiency (%)	Adsorption capacity (mg/g)	Isotherm model	Ref
Poly(vinylidene fluoride)/polyethylene oxide (PVDF/PEO)	Montmorillonite	Malachite green	95.40	33.4	Langmuir	Ali and Ismail [4]
Poly-epichlorohydrin-dimethylamine	Natural attapulgite	Reactive black 5	Not given	237.4	Langmuir	Guo et al. [20]
		Reactive red 239	Not given	228.3		
Quaternized polyacrylonitrile	Montmorillonite	Methylene blue	99.70	Not given	Freundlich	Kenawy et al. [24]
Chitosan/alginate	Dodecyl amine modified clay (kaolinite)	Methylene blue	Not given	73.1		Khan et al. [26]
		Acid black	Not given	71.5		
Ethylene diamine (EDA)-trimesoyl chloride (TMC) polymer	Diatomite	Rhodamine B	Not given	371.8	Non-linear Langmuir	Saleh et al. [43]
Polystyrene	Kaolin	Methylene blue	Not given	Not given		Khalil and Kenawy [25]
Poly(acrylamide-*co*-acrylic acid)/sodium alginate	Montmorillonite	Methylene blue	Not given	530.7	Pseudo two-order kinetic model and Freundlich isotherm mode	Wang et al. [51]
Polyvinyl alcohol (PVA) and alginate	Bentonite	Methylene blue	90	51.34	Langmuir	Aljar et al. [5]
Polyaniline	Montmorillonite	Acid green 25	100	Not given	Pseudo-second-order kinetic model	Kalotra and Mehta [23]
Chitosan-grafted-hydrolyzed polyacrylamide	Montmorillonite	Basic red 46	78	1813	Langmuir	Ferfera-Harrar [18]

inorganic chemical manufacturing industry, coating industry, battery manufacturing, and recycling industry is very significant and has become a global issue. As a result, more attention has been placed on the removal of these toxic heavy metals (Cu, Pb, Ni, Cd, Cr, Sb, Se, and U) with the discoveries of their potential to cause health issues: skin diseases, neurological disorders, respiratory problems, and the like [34, 42]. However, compared to the research studies on the development of clay/polymer adsorbents for the removal of dyes, much fewer studies have been done on using clay/polymer composites to remove heavy metals for the past couple of years. Some of the clay/polymer adsorbents developed are summarized in Table 2.

As discussed previously, one of the advantages of combining polymers and clay minerals in developing adsorbents is their potential to remove a broad range of contaminants. Kong et al., in 2019, have developed Lignin xanthate resin and bentonite clay (LXR-BT) composite as an adsorbent to remove organic pollutants and heavy metals in water. They tested the developed material with doxycycline hydrochloride antibiotic (DCH) and mercury ions (Hg(II)) in water. The developed LXR-BT adsorbent has shown 438.75 and 36.45 mg/g adsorption capacity for DCH and Hg(II), respectively. In contrast, pristine Bentonite has only shown 119.93 and 21.29 mg/g adsorption capacity for DCH and Hg(II), respectively. Therefore, it is evident that the clay/polymer composite has enhanced the adsorption capacity more than the pristine clay mineral alone (Table 3).

Table 2 Clay/polymer adsorbents for the removal of heavy metals from the wastewater

Polymer	Clay mineral	Heavy Metal Ion	Removal efficiency (%)	Adsorption capacity (mg/g)	Isotherm/ Kinetic model	Ref
Chitosan/ alginate	Dodecyl amine modified clay (kaolinite)	Cr (VI)	Not given	62.4		Khan et al. [26]
Lignin xanthate resin	Bentonite clay	Hg(II)	Not given	36.45	Langmuir	Kong et al. [29]
Polyacrylamide	Attapulgite	Ni(II)	Not given	64.3	Langmuir	Li et al. [32]
Xanthan Gum/ Poly(acrylic acid)	Cloisite 15A	Co^{2+}	45	436.62	Pseudo second order model	Esmaeildoost et al. [15]
		Cu^{2+}		530.14		
		Ni^{2+}		511.74		
Polypyrrole	Montmorillonite	Cr(VI)	80			Mdlalose et al. [35]
Cu^{2+} imprinted polymer	Montmorillonite	Cu^{2+}	Not given	23.6	Langmuir	Msaadi et al. [38]

Table 3 Clay/polymer composites for the removal of organic pollutants from the wastewater

Polymer	Clay mineral	Organic Pollutant	Removal efficiency (%)	Adsorption capacity	Isotherm/ Kinetic model	Ref
Lignin xanthate	Bentonite clay	Organic doxycycline hydrochloride	Not given	438.75 mg/g	Langmuir model	Kong et al. [29]
Chitosan	Organic-clay Dellite 43 B	Carbendazim	Not given	0.4618 mg/g	Langmuir model	Baigorria and Fraceto [9]
Cyclodextrin polymer (Fe − MMT − βcd − DFB)	Iron coated Montmorillonite	Bisphenol A	95	0.272 mmol/g	Langmuir model	Kundu et al. [31]
		Carbamazepine		0.391 mmol/g		
		Perfluorooctanoic acid		0.047 mmol/g		

4.3 *The Removal of Organic Pollutants*

The release of organic pollutants into the surrounding water resources by industries has also caused an alarming crisis in today's world. The release of phenol and phenolic compounds, aromatic molecules, pesticides, oils, and other toxic organic compounds with industrial wastewater into the environment without proper treatment has exposed humans and animals to various health issues, including cancer, neurological disorder, and endocrine disruptions [39, 40, 42, 1].

However, the use of clay minerals as adsorbents for organic pollutants has been limited due to their hydrophilic nature. In contrast, polymeric adsorbent seems to be the most effective, being hydrophobic and able to modify with functional groups compatible with the contaminants. As with the adsorbents developed for the removal of heavy metals, there has been only a handful of research studies on the use of clay/polymer composites for the removal of organic pollutants; some of them are summarized in Table 3.

The research study carried out by [31] is another example of the use of clay/polymer composite to remove a broad range of contaminants. They have developed an iron-montmorillonite-cyclodextrin composite for bisphenol A (BPA), carbamazepine (CMZ), and perfluorooctanoic acid (PFOA) adsorption. The developed clay/polymer adsorbent by [31] has shown 0.272, 0.391, and 0.047 mmol/g Langmuir maximum adsorption capacity for BPA, CBZ, and PFOA, respectively.

5 Challenges and Future Prospects

As expected, clay/polymer adsorbents outperform pristine clay minerals or polymeric adsorbents alone. The low cost, ease of processing, ability to modify accordingly, and most importantly, ability to adsorb a broad range of contaminants make these clay/polymer nanocomposites exceptional adsorbents. These economically beneficial, efficient, and effective adsorbents seem to be the potential solution to reduce the untreated wastewater released into the environment in low-income countries [6].

The research studies [28, 38] on developing various clay/polymer adsorbents to remove industrial effluents show that these adsorbents perform exceptionally well on the laboratory scale. However, it is essential to study the performance of these adsorbents on a large scale. The lack of studies on large-scale performance is a crucial limitation that needs to be overcome to develop these adsorbents into promising wastewater tools in real life. The other factor that needs to be considered is increasing the reusability of the developed adsorbents while making them environmentally friendly and economically beneficial. The studies related to the reusability of clay/polymer composites as wastewater treatment tools are very limited.

Moreover, as observed in the literature [15, 20, 31], these clay/polymer nanocomposites can be designed to adsorb various industrial pollutants at once. Therefore, taking advantage of the combined properties of clay minerals and polymers, it might be more beneficial to look into developing a universal adsorbent for industrial contaminants. This type of adsorbent developed using abundant, cheap clay minerals, and easily modifiable polymers would be more beneficial for developing wastewater treatment solutions for low-income countries and a solution for the current water scarcity.

On the other hand, polymers are flexible and easily manipulable while being easily processable, clay/polymer composites can be designed as any structure: film, membrane, solid, aerogel, porous network, and the like [39]. Because of all these phenomenal characteristics, clay/polymer adsorbents could be developed into an adsorbent used at an industrial level.

6 Conclusion

Even though various advanced wastewater treatment methods are developed, untreated wastewater is still released into the environment in large quantities, especially in low-income countries. Therefore, developing affordable yet efficient pollutant removal techniques for water purification is essential. That is why adsorption has been given significant attention. Among various adsorbents, clay/polymer adsorbents seem to have the potential to be ultimate adsorbents because of their exceptional properties: easy processability can be modified easily, high surface area, high adsorption efficiency, and capacity compared to their original self, ability to adsorb a broad range of contaminants and regenerable without the loss of adsorption properties are some of them. Moreover, with these properties and wide varieties of polymers and clay minerals available, there are endless possibilities for developing efficient and effective clay/polymer adsorbents for industrial effluents. However, in the next couple of years, immense attention must be drawn to scaling up the lab-scale discoveries and development that have already been done on so many different types of clay/polymer composites for wastewater treatments. Otherwise, this valuable and affordable wastewater treatment tool would not be realized.

References

1. Abeysinghe, H., Etampawala, T.: MWCNT Buckypaper as electrochemical sensing platform: a rapid detection technology for phthalic acid esters in solutions. ChemistrySelect **7**, e202201900 (2022)
2. Ahmed, J., Thakur, A., Goyal, A.: Chapter 1. Industrial Wastewater and Its Toxic Effects. Biol. Treat. Ind. Wastewater, (2021)
3. Alekseeva, O.V., Noskov, A.V., Agafonov, A.V.: Structure, physicochemical properties, and adsorption performance of the ethyl cellulose/bentonite composite films. Cellulose (Lond) **29**, 3947–3961 (2022)
4. Ali, H., Ismail, A. M.: Developing montmorillonite/PVDF/PEO microporous membranes for removal of malachite green: adsorption, isotherms, and kinetics. J. Polym. Res. **28**, (2021)
5. Aljar, M.A.A., Rashdan, S., Abd El-Fattah, A.: Environmentally friendly polyvinyl alcohol-alginate/bentonite semi-interpenetrating polymer network nanocomposite hydrogel beads as an efficient adsorbent for the removal of methylene blue from aqueous solution. Polymers (Basel), **13**, (2021)
6. Amari, A., Mohammed Alzahrani, F., Mohammedsaleh Katubi, K., Salem Alsaiari, N., Tahoon, M. A., Ben Rebah, F.: Clay-polymer nanocomposites: preparations and utilization for pollutants removal. Materials (Basel) **14**, (2021)
7. AYALEW, A. A.: A critical review on clay-based nanocomposite particles for application of wastewater treatment. Water Sci Technol **85**, 3002–3022 (2022)
8. Azha, S. F., Ismail, S.: Feasible and economical treatment of real hand-drawn batik/textile effluent using zwitterionic adsorbent coating: Removal performance and industrial application approach. J. Water Process. Eng. **41**, (2021)
9. Baigorria, E., Fraceto, L.F.: Novel nanostructured materials based on polymer/organic-clay composite networks for the removal of carbendazim from waters. J. Clean. Prod. **331**, (2022)
10. BERBER, M. R.: Current advances of polymer composites for water treatment and desalination. J. Chem. **2020**, 1–19 (2020)
11. Das, P., Manna, S., Behera, A.K., Shee, M., Basak, P., Sharma, A.K.: Current synthesis and characterization techniques for clay-based polymer nano-composites and its biomedical applications: A review. Environ Res **212**, 113534 (2022)
12. Dharmapriya, T.N., Li, D., Chung, Y.C., Huang, P.J.: Green synthesis of reusable adsorbents for the removal of heavy metal ions. ACS Omega **6**, 30478–30487 (2021)
13. Dieu le, T., Vinh Tran, H.: Graphene oxide-based adsorbents for organic-dyes removal from contaminated water: A review. Z. Für Anorg. Und Allg. Chem. **648**, (2022)
14. Dutta, D., Arya, S., Kumar, S.: Industrial wastewater treatment: Current trends, bottlenecks, and best practices. Chemosphere **285**, 131245 (2021)
15. Esmaeildoost, F., Shahrousvand, M., Goudarzi, A., Bagherieh-Najjar, M.B.: Optimization of Xanthan Gum/Poly(acrylic acid)/Cloisite 15A Semi-IPN hydrogels for heavy metals removal. J. Polym. Environ. **30**, 4271–4286 (2022)
16. FAO, F. A. A. O. O. T. U. N.: Aquastat main database, (2019)

17. Fei, Y., Hu, Y.H.: Design, synthesis, and performance of adsorbents for heavy metal removal from wastewater: a review. J. Mater. Chem. A. **10**, 1047–1085 (2022)
18. Ferfera-Harrar, H., Benhalima, T., Sadi, A.: Development of functional chitosan-based superabsorbent hydrogel nanocomposites for adsorptive removal of Basic Red 46 textile dye. Polym. Bull. **79**, 6141–6172 (2021)
19. Gkika, D.A., Mitropoulos, A.C., Kyzas, G.Z.: Why reuse spent adsorbents? The latest challenges and limitations. Sci. Total. Environ. **822**, 153612 (2022)
20. Guo, H., Xia, K., Cao, M., Zhang, X.: Surface modification of attapulgite by grafting cationic polymers for treating dye wastewaters. Materials (Basel), **14**, (2021)
21. Iravani, R., An, C., Adamian, Y., Mohammadi, M.: A review on the use of nanoclay adsorbents in environmental pollution control. Water, Air, & Soil Pollut. **233**, (2022)
22. Jones, E.R., van Vliet, M.T.H., Qadir, M., Bierkens, M.F.P.: Country-level and gridded estimates of wastewater production, collection, treatment and reuse. Earth Syst. Sci. Data **13**, 237–254 (2021)
23. Kalotra, S., Mehta, R.: Synthesis of polyaniline/clay nanocomposites by in situ polymerization and its application for the removal of Acid Green 25 dye from wastewater. Polym. Bull. **78**, 2439–2463 (2020)
24. Kenawy, E.-R., Tenhu, H., Khattab, S. A., Eldeeb, A.A., Azaam, M.M.: Highly efficient adsorbent material for removal of methylene blue dye based on functionalized polyacrylonitrile. Eur. Polym. J. **169**, (2022)
25. Khalil, A.M., Kenawy, S.H.: Hybrid membranes based on clay-polymer for removing methylene blue from water. Acta Chim. Slov. **67**, 96–104 (2020)
26. Khan, M. N., Chowdhury, M., RAHMAN, M. M.: Biobased amphoteric aerogel derived from amine-modified clay-enriched chitosan/alginate for adsorption of organic dyes and chromium (VI) ions from aqueous solution. Mater. Today Sustain. **13**, (2021)
27. Khan, S. A., Khan, T. A.: Clay-hydrogel nanocomposites for adsorptive amputation of environmental contaminants from aqueous phase: A review. J. Environ. Chem. Eng. **9**, (2021)
28. Kinoti, I.K., Karanja, E.M., Nthiga, E.W., M'Thiruaine, C.M., Marangu, J.M., Vosoughi, M.: Review of clay-based nanocomposites as adsorbents for the removal of heavy metals. J. Chem. **2022**, 1–25 (2022)
29. Kong, Y., Wang, L., Ge, Y., Su, H., Li, Z.: Lignin xanthate resin-bentonite clay composite as a highly effective and low-cost adsorbent for the removal of doxycycline hydrochloride antibiotic and mercury ions in water. J Hazard Mater **368**, 33–41 (2019)
30. Kumari, N. M., Chandra.: Basics of clay minerals and their characteristic properties. Clay and Clay Minerals. IntechOpen, London, UK(2021)
31. Kundu, S., Korin Manor, N. Radian, A.: Iron-montmorillonite-cyclodextrin composites as recyclable sorbent catalysts for the adsorption and surface oxidation of organic pollutants. ACS Appl Mater Interfaces. **12,** 52873-52887(2020)
32. Li, J., Zheng, Y., Feng, X., Lv, C., Liu, X., Zhao, Y., Chen, L.: Adsorption removal of Ni(II) and phenol from aqueous solution by modified attapulgite and its composite hydrogel. Environ Technol **42**, 2413–2427 (2021)
33. López-Rodríguez, D., Micó-Vicent, B., Jordán-Núñez, J., Bonet-Aracil, M. and Bou-Belda, E.: Uses of nanoclays and adsorbents for dye recovery: a textile industry review. Appl. Sci. **11**, (2021)
34. Mao, S., Gao, M.: Functional organoclays for removal of heavy metal ions from water: A review. J. Mol. Liq. **334**, (2021)
35. Mdlalose, L., Balogun, M., Setshedi, K., Chimuka, L., Chetty, A.: Performance evaluation of polypyrrole–montmorillonite clay composite as a re-usable adsorbent for Cr(VI) remediation. Polym. Bull. **78**, 4685–4697 (2020)
36. Mohapi, M., Sefadi, J.S., Mochane, M.J., Magagula, S.I. and Lebelo, K.: Effect of LDHs and other clays on polymer composite in adsorptive removal of contaminants: A review. Crystals, 10, (2020)
37. Mok, C.F., Ching, Y.C., Muhamad, F., Abu Osman, N.A., Hai, N.D. and Che Hassan, C.R.: Adsorption of dyes using Poly(vinyl alcohol) (PVA) and PVA-based polymer composite adsorbents: A review. J. Polym. Environ. **28,** 775–793 (2020)

38. Msaadi, R., Yilmaz, G., Allushi, A., Hamadi, S., Ammar, S., Chehimi, M.M., Yagci, Y.: Highly selective copper ion imprinted clay/polymernanocomposites prepared by visible light initiated radical photopolymerization. Polymers (Basel), **11**, (2019)
39. Al-Shahrani, A., Taie, I., Fihri, A., Alabedi, G.: Polymer-clay nanocomposites for corrosion protection. In: Current topics in the utilization of clay in industrial and medical applications; IntechOpen: London, UK, pp. 61–79 (2018)
40. Mukhopadhyay, R., Sarkar, B., Palansooriya, K.N., Dar, J.Y., Bolan, N.S., Parikh, S.J., Sonne, C., Ok, Y.S.: Natural and engineered clays and clay minerals for the removal of poly- and perfluoroalkyl substances from water: State-of-the-art and future perspectives. Adv. Colloid. Interface. Sci **297**, 102537 (2021)
41. Quanz, M. E., Walker, T. R., Oakes, K., Willis, R.: Effects of industrial effluent on wetland macroinvertebrate community structures near a wastewater treatment facility. Ecol Indic **127**, (2021)
42. Rajak, S., Raza, S., Tewari, A., Sinha, R.A.: Environmental toxicants and NAFLD: A neglected yet significant relationship. Dig Dis Sci **67**, 3497–3507 (2022)
43. Saleh, T.A., Tuzen, M., Sari, A.: Evaluation of poly(ethylene diamine-trimesoyl chloride)-modified diatomite as efficient adsorbent for removal of rhodamine B from wastewater samples. Environ Sci Pollut Res Int **28**, 55655–55666 (2021)
44. Saravanakumar, K., de Silva, S., Santosh, S.S., Sathiyaseelan, A., Ganeshalingam, A., Jamla, M., Sankaranarayanan, A., Veeraraghavan, V.P., Mubarakali, D., Lee, J., Thiripuranathar, G., Wang, M.H.: Impact of industrial effluents on the environment and human health and their remediation using MOFs-based hybrid membrane filtration techniques. Chemosphere **307**, 135593 (2022)
45. Shaikh, T. M. A.: Adsorption of Pb(II) from wastewater by natural and synthetic adsorbents. Biointerface Res. Appl. Chem. **10,** 6522-6539(2020)
46. Sharma, A., Mangla, D., Shehnaz, Chaudhry, S. A.: Recent advances in magnetic composites as adsorbents for wastewater remediation. J. Environ. Manage **306,** 114483(2022)
47. Shi, Y., Zhong, S., Wang, X., Feng, C.: A review of the removal of heavy metal ions in wastewater by modified montmorillonite. Water Policy, (2022)
48. UNITEDNATIONS: The United nations world water development report 2021: Valueing water. UNESCO, Paris (2021)
49. UNWATER.: United Nations world water development report 2017. Wastewater: The Untapped Resource. WWAP (United Nations World Water Assessment Programme). Paris: UNESCO(2017)
50. UNWATER 2019. United Nations world water development report: Leaving no one behind WWAP (UNESCO World Water Assessment Programme). UNESCO, Paris (2019)
51. Wang, T., Yan, L., He, Y., Alhassan, S.I., Gang, H., Wu, B., Jin, L., Wang, H.: Application of polypyrrole-based adsorbents in the removal of fluoride: a review. RSC Adv. **12**, 3505–3517 (2022)
52. Wang, W., Fan, M., Ni, J., Peng, W., Cao, Y., Li, H., Huang, Y., Fan, G., Zhao, Y., Song, S.: Efficient dye removal using fixed-bed process based on porous montmorillonite nanosheet/poly(acrylamide-co-acrylic acid)/sodium alginate hydrogel beads. Appl. Clay Sci., 219, (2020b)
53. Zhang, T., Wang, W., Zhao, Y., Bai, H., Wen, T., Kang, S., Song, G., Song, S., Komarneni, S.: Removal of heavy metals and dyes by clay-based adsorbents: From natural clays to 1D and 2D nano-composites. Chem. Eng. J. 420, (2020)

Clays and Their Polymer Nanocomposites

Padmaja Sudhakar, Radhika Rao, Hetvi Dave, and Virang Vasveliya

Abstract Clean drinking water resources are scanty in many regions of the world due to contamination with several organic and inorganic pollutants. Amongst the numerous techniques of contaminant removal, adsorption is the most economic and efficient technique. Though the low cost and readily available clay minerals have been considered as adsorbents of choice, their practical use as adsorbents is limited due to their low adsorption tendency towards organic species, difficulty in regeneration and recovery. Clay–polymer composites combining the advantageous characteristics of clay minerals and polymers have emerged as attractive alternative with high adsorption efficiency, surface area, and renderability. This chapter describes the different classes of clays and polymers used, physicochemical and structural properties of clay–polymer composites, synthetic methodologies, and characterization techniques as well as the main applications in the field of environmental remediation. Finally, the different mechanisms involved in the adsorption phenomena will be discussed.

1 Introduction

Clay refers to the group of materials made up of layered silicates or clay minerals with traces of metal oxides and organic matter. The basic building unit of clay minerals is composed of tetrahedral silicates and octahedral hydroxide sheets arranged in 1:1

P. Sudhakar (✉) · R. Rao · H. Dave · V. Vasveliya
Faculty of Science, Department of Chemistry, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India
e-mail: padmaja.sudhakar-chem@msubaroda.ac.in

P. Sudhakar
Faculty of Science, Department of Environmental Studies, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_15

ratio (e.g. kaolinite and serpentine) and 2:1 (e.g. smectite, chlorite, and vermiculite). Depending on the charge the clay particles can be divided into cationic clay minerals and anionic clay minerals [1].

The clay ingredients are split into two categories based on how the alternating sheets of “SiO_2” and “AlO_6” units are arranged. First category is 2:1 clay (smectite, and vermiculite) and second is 1:1 clay (Kaolinite). Usually, 2:1 clay is used rather than 1:1 because they lack the effective intercalation properties, and the separation of layers becomes difficult. This leads to increased charge density which makes the penetration of the layers difficult [2].

Classification of clay

Based on the source, clay is categorized as (1) natural clay and (2) synthetic clay. The clay material comprises SiO_2 and AlO_6 in their composition and arranged in an alternative way. Two-dimensional arrays of Si–O- tetrahedral and 2D arrays of Al or Mg-O-OH octahedral are the main constituents of clay minerals. These sheets of tetrahedral and octahedral structure are stacked in various ways in the majority of clay minerals. They are classified into (a) 2:1 and (b) 1:1 clay type.

a. Tetrahedral sheet structure

The Si atoms are coordinated with four oxygen atoms in Si–O sheets. A typical tetrahedron has the Si atom in its middle, with the O atoms placed on its four corners. Each tetrahedron in the sheet shares three of its four oxygen atoms with three of its neighbours. Each tetrahedron’s fourth oxygen atom faces downward. Tetrahedral sheets or silica sheets are other names for this Si–O sheet [3].

b. Octahedral sheet structure

The Al, Mg-O-OH sheets have a hexagonal close packing because the Al or Mg atoms are coordinated with six oxygen atoms or -OH groups, which are positioned around the Al or Mg atom and with their centres on the corners of a regular octahedron. The octahedral sheet shares the fourth oxygen atom that sticks out of the tetrahedral sheet. As 1:1 layer minerals, this atom sharing may take place between silica and an alumina sheet. In 2:1 layer minerals, two silica sheets on either side of an alumina or magnesia sheet share oxygen atoms. In clay minerals, these layers are layered one on top of the other [4]. Clay in nature is hydrophilic. It is necessary to alter the clay’s surface so that hydrophobic polymers can interact with it. The interlayers of the clay are held via strong covalent bonds which makes dispersion difficult, to avoid all these problems the clay particles are modified before dispersion in the polymer matrices which also increases the interlayer spacing. There is an overall improvement of all the properties such as mechanical, thermal, optical, and barrier properties.

Clays have a special property that allows them to exchange cations between each of their layers and retain them. The cation exchange method is typically used to modify the surface of clay. By treating additional cations in solution, the intercalated cations can be replaced by other cations. The highest number of cations that may be continuously taken up by a particular volume of clay is known as the cation exchange capacity. The adsorption capacity of montmorillonite is governed by its capacity for cation exchange in the interlayer region. Inorganic ions (primarily Na^+, Ca^{2+}, Mg^{2+}, and K^+), amines, amino acids, cationic surfactants, and non-ionic surfactants are the most exchangeable cations that can be adsorbed on the clay surface via the cation exchange process. The Langmuir-Blodgett reaction between hybrid monolayers of clay mineral and amphiphilic alkyl amino cation can also make the clay surface organophilic. The negatively charged clay platelets in the suspension are adsorbed onto a floating monolayer of the amphiphilic alkyl ammonium cation at an air–clay suspension interface when a solution of the cation is distributed onto the suspension of clay. To create a hybrid multilayer, one can transfer the hybrid monolayers of clay platelets and alkylammonium cations generated at the interface onto a solid surface [3, 5].

Modification can also be achieved by using organic modifiers which leads to high mechanical and thermal properties as well as enhanced liquid barrier properties [6]. Other type of modification includes the formation of composite. When two or more materials, each having their own significant characteristic properties combines to form a new substance with superior properties than the original it is called a composite. Figure 1 summarizes the types of clay composites in which primarily the polymer-based and non-polymer-based materials are used for modification [7]. The layered clays have strong intralayer covalent bonds within the individual sheets which poses a difficulty in dispersion of the clay in polymer matrix during preparation of clay–polymer hybrid composites, thus requiring modification of the clay to form nanocomposites with the polymers. The polymers mentioned are few representative polymers and not exhaustive. Others are mentioned at the appropriate place in the chapters.

As per the work done previously and reported by various authors grafting polar functional groups onto the polymer chains is one of the methods of choice for the polymers which lack functional groups. The best example for this is maleic anhydride which is used for grafting onto PP which then tends to produce clay/PP nanocomposites. Usually, when the clay and the polymer are compatible with each other the intercalation between the two takes place easily without the need of any pre-treatment. Most of the polymers available tend to be hydrophobic and generally are not compatible with hydrophilic clays. The clay used has a thickness of 1 nm and the side dimensions which fall between the range of 30 nm to a few micro-metres which totally depends on the clay. The Van der Waals forces and the weak electrostatic forces are the ones responsible between the interlayers and for the stacking of the various layers. Inside the layers the aluminium ions of the layers can be replaced with iron or magnesium or lithium ions so there is charge neutralization.

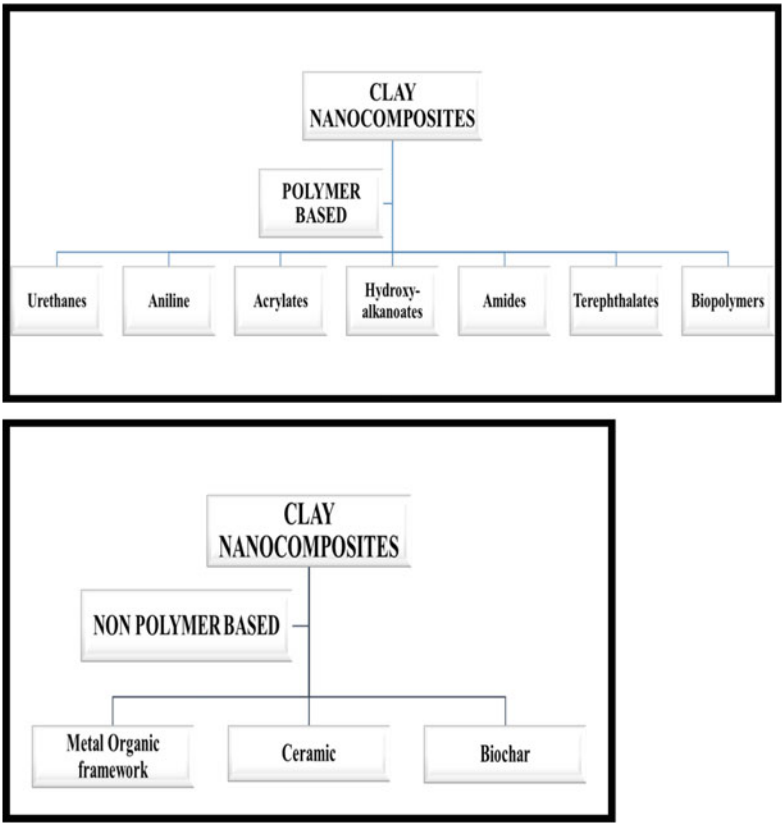


Fig. 1 Types of clay composites based on the materials used for modification

2 Clay and Their Polymer Nanocomposites

The functionality of polymers and clays can be increased by the formation of composites. The composite structure has properties like stiffness, strength, high resistance to fatigue as well as corrosion, low coefficient of expansion, and ease in manufacturing. The polymer-based composites are advantageous in terms of enhancement of the clay properties. Clay possesses some specific physicochemical properties such as high surface reactivity, optimal rheological properties, swelling and colloidal capacity, and high water dispersibility which render them suitable for many environmental remediation applications [8]. The lower clay content and lower weight of clay in the composites add to the advantage of the material. The composites thus exhibit improved biodegradability, tensile strength, modulus, and flexural characteristics that are beneficial for removing pollutants.

When these are scaled down to the nano range, they become nanocomposites. Out of the combining constituents any one of the constituents when has a nanoscale range then the material is termed to be a nanocomposite. These nanocomposites provide the additional benefit of more surface area, and there is an improvement in the electrical as well as the optical properties. The chemical resistance of these materials is also high and the flame retardancy is also enhanced when compared to simple composite materials [9]. The clay minerals have low price, accessibility, high aspect ratio in the nanoform which offer excellent properties at low loadings, thus keeping the intrinsic benefits of polymer matrix and clay intact.

The modified/intercalated clay–polymer composites have enhanced properties than that of the polymer matrix. Due to the rigid clay structure and high aspect ratio, there is an increase in the stiffness and modulus of polymer matrix, thus increasing its mechanical strength. The increase in the filler volume also contributes to the tensile modulus [2, 10, 11]. The thermal properties of the polymer matrix are enhanced on incorporation of clay particles. All these properties make the clay–polymer composites as compatible adsorbents against the removal of many organic and inorganic species in water bodies. The layered structure of clay has the ability to retain water in the interlayer spacing resulting in heavy metal adsorption and ion exchange. The aspect ratio of clay spread in the polymer matrix also shows an impact on the gas barrier properties [2].

Figure 2 shows the various clays and few representative polymers that have been widely used to form clay–polymer nanocomposites and are summarized in Table 1.

2.1 Types of Polymer Clay Morphologies

The polymer and clay can adopt any of these morphologies—phase-separated, intercalated, and exfoliated [1, 12]. Phase-separated composite structure results when the interaction between the clay and the polymer composite is very weak which does not allow the intercalation of the polymer matrix in the clay composite but results in a structure where the polymer chain surrounds the clay. Due to this, there is not separation between the clay platelets. This may result in large-sized polymer/clay composites which may be of the size of microns. The intercalated clay composites result when some of the polymer chains have penetrated the individual clay platelets. This enhances the interlayer distance between the clay layers. Polymer–clay compatibility is crucial for the success of polymer nanocomposites' qualities when clay is used as reinforcement. An approach for the compatibilization of organic material with an inorganic is claimed via the intercalation of organic components in layered inorganic clays [13].

The exfoliated nanocomposites are completely separated clay nanoplatelets which are homogeneously dispersed in the polymer matrix. The exfoliated composites are the one producing the highest surface area which results in the enhancement of various physicochemical properties of the composites [1]. The exfoliation/intercalation increases the stiffness and modulus of the nanocomposites.

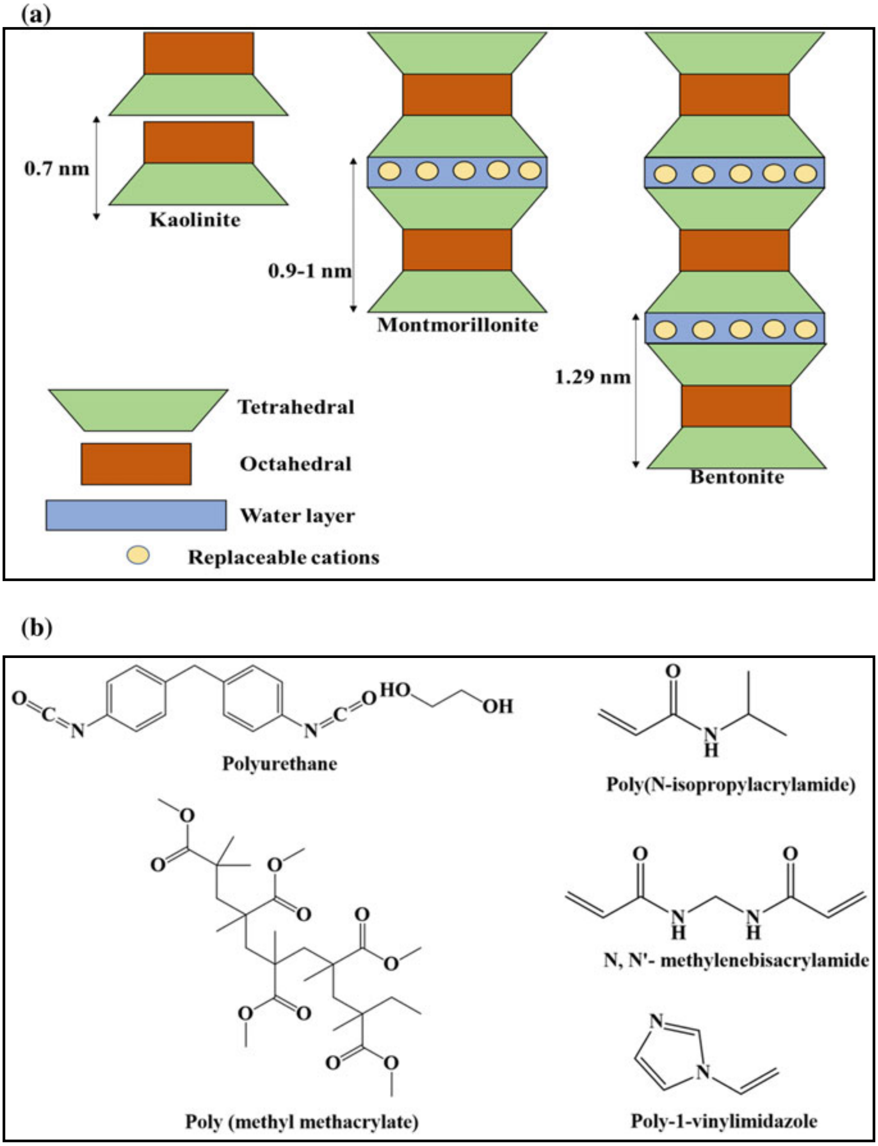


Fig. 2 **a**) Various types of clays and **b**) various polymers generally used in the formation of clay–polymer nanocomposites

Table 1 Classes of clay–polymer composites

Classes	Structure	Polymer (General examples)
1 1:1 clays		
Kaolinite	Two-sheet phyllosilicates	Poly(hydroxyl alkanoate).Imidazole, Resorcinol–formaldehyde polymer blends, Chitosan
1 2:1 clays		
Hectorite	Layered silicates	Poly(N-isopropylacrylamide) (PNIPAm)
Montmorillonite	Two tetrahedral sheets	Biopolymer, Chitosan, Polystyrene, Epoxy resin. Natural rubber, Chitosan-polyacrylic acid. Alginate-Aniline, p-cylcodextrine
Bentonite	Lamellar structure	Caprolactam (PA-6), Polystyrene, Phosphatidydylcholine, Chitosan, Poly(vinylalcohol)
Vermiculite	Expanding three sheet phyllosilicates	Poly(vinylalcohol), Polyurethane, Poly(Lactic acid), Chitosan
Sepiolite	Sheet-fibrous structure	Polyamides, Polymethylmethacrylate (PMMA), Polyethylene terephthalate, Biobased Polyamide, Caprolactam (PA-6)

Figure 3 shows the schematic in which the clay/polymer hybrid composites are classified on the basis of the interactions between the clay and the polymer layers to adopt different morphologies.

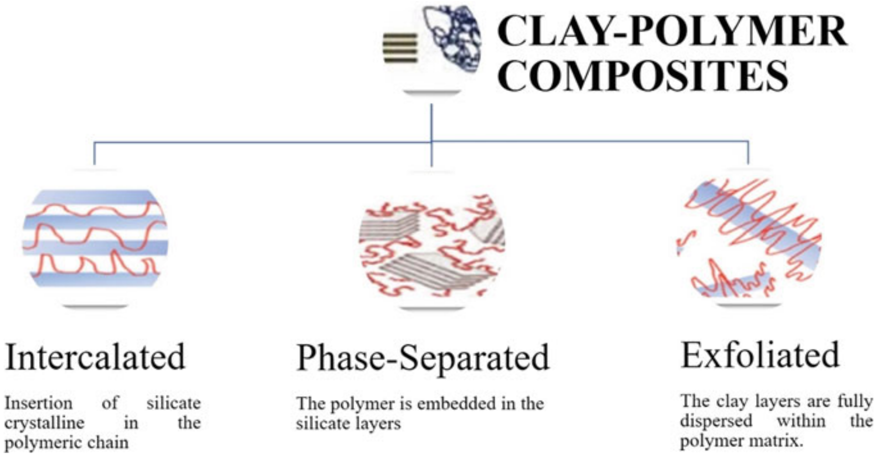


Fig. 3 Classification of clay–polymer composites based on morphologies [2]

2.2 *Different Categories of Clays Used to Synthesize Clay–Polymer Nanocomposites*

(a) **Montmorillonite-based polymer nanocomposites**

Montmorillonite (MMT), a commonly used clay, with general formula $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$ belongs to the family of 2:1 phyllosilicate. It is a hydrophilic clay which is compatible with polymers like polyaniline (PANI). It has advantages of being naturally abundant and has abundant exchangeable surface charges and has the property of layer exfoliation [11]. Montmorillonite is a potential adsorbent of several cations and organic compounds due to its high cation exchangeability, Bronsted and Lewis type of acidity, huge surface area, chemical and physical stability, and layer structure.

Nanocomposites (NC) comprising MMT and polymer are reported to display greater toughness and strength [3, 13]. Montmorillonites exchanged with chain onium ions having more than 12 carbon atoms demonstrated an interesting benefit. Synthesis of nanocomposites NC with MMT clay phase intercalated in the cross-linked polyurethane network was achieved by the polymerization process of polyol isocyanate precursor and organoclay. The onium ion's structure and length had a significant impact on the intercalation process [14].

Hybrids of cellulose nanofibrils and MMT nanoplatelets are another interesting NCs that are reported to exhibit outstanding mechanical performance along with other features such as minimal oxygen permeability, thermal shielding, and fire retardancy. Optimal properties as compared to their pristine counterparts was achieved due to the aggregation and formation of multi-layered cellulose nanofibrils, MT NC with a weight ratio of 50:50 [15–17].

(b) **Laponite-based polymer nanocomposites**

Laponite is made up of octahedral layers of tetrahedral silica intercalated with layers of Mg^{2+} and Li^+ ions with a composition $Na^+_{0.7}[(Mg_{5.5}Li_{0.4})\ Si_8O_{20}(OH)_4]^{0.7}$. It displays a unit cell that resembles a disc and has a diameter of approximately 25 nm and a thickness of 1 nm. The silanol groups (SiO-), which are negatively charged as well as the groups formed by hydroxyl (MgOH and LiOH), augment the sorption capabilities of laponite-based clay nanocomposites. Depending on the pH of the surrounding solution, they could become positively or negatively charged.

The pH and temperature sensitive "smart" hydrogels such as polymethacrylic acid hydrogel are widely used in agricultural and biomedical fields as delivery methods for controlled release of drugs, fertilizers, and pesticides. Hydrogels do, however, have several drawbacks, such as poor mechanical and adsorption qualities. Incorporation of inorganic components, like clays, into the structure of these hydrogels are reported to alleviate these difficulties [18].

(c) **Sepiolite-based polymer nanocomposites**

Sepiolite, a magnesium phyllosilicate $[Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4 8(H_2O)]$, has two layers of silica arranged in a tetrahedron and a layer of magnesium ions with octahedral coordination to form threefold strips. The strips are arranged to form channels with water molecules. The presence of these channels significantly increases the specific surface area of sepiolite by 200–300 m^2/g.

Polyamide-6 is a widely used thermoplastics in various industries such as electrical, automobile, and electronic, owing to the excellent mechanical properties. Nevertheless, the crack sensitivity, dimensional instability, and high moisture sorption reduced structural parts applications. Sepiolite had been introduced into the polymer matrix to enhance the mechanical, predominantly tensile and flexural strength and improve thermal properties [19, 20]. The majority of earlier research focused on using macro-size sepiolite as a beneficial filler in thermoplastics to form composites is now being replaced by nano-sized sepiolite. Furthermore, the sepiolite surface may be modified to improve its interaction with the chains of polyamide to improve the composite properties compared to the sepiolite of the unmodified surface. Asensio. M *et al.* investigated the effects of sepiolite orientation and concentration on the morphological, mechanical, and thermal properties of polyamide for structural applications in the automotive sectors [21].

Similarly, polymethyl methacrylate, an acrylic resin has poor thermal and mechanical properties could be improved by formation of composite with sepiolite [19].

(d) Hectorite-based polymer nanocomposites

Hectorite ($Na_{0.3}(Mg,Li)_3Si_4O_{10}(OH)_2$) is a trioctahedral smectite clay having an elongated platelet structure with an intrinsic negative charge balanced by exchangeable sodium (Na^+) ions with thickening properties. The hectorite clay provides large surface area and enhances the mechanical properties of the composite in which it is incorporated. A well-known temperature-responsive polymer poly(N-isopropylacrylamide) (PNIPAm) with hectorite as a filler has led to successful reinforcement composite [22].

(e) Bentonite clay–polymer nanocomposites

Chemical formula of Bentonite clay is $Al_2H_2Na_2O_{13}Si_4$. The surface hydroxyl groups and the structural permanent negative sites of bentonite clay particles each carry a separate type of electrical charge, which contributes to their capacity for cation exchange. The ability of some metal ions to enter their crystal lattice and alter their surface charge with interlayer complexation ability is well recognized.

The applicability of clay can be improved by formation of a composite with polymers such as acrylic acid [23]. To prepare the composite firstly acrylic acid was treated with base to give acrylamide followed by cross-linking with bentonite clay via N, N'- methylenebisacrylamide. The polymerization reaction was carried out at 70 ºC in the presence of $(NH_4)S_2O_8$ under nitrogen atmosphere to produce the nanoclay–polymer composite. The formation of composite was confirmed by Fourier transform infrared spectroscopy, scanning electron microscopy, and X-ray diffraction that indicated complete dispersion and exfoliation of the bentonite layers in the composite, leading to an increase of the surface area with applicability in agriculture and environmental remediation.

(f) **Kaolinite clay–polymer nanocomposites**

Kaolinite (Al_2O_3 $2SiO_2.2H_2O$), a layer type 1:1 clay mineral, is made up of silicate sheets (Si_2O_5) joined to layers of aluminium oxide/hydroxide ($Al_2(OH)_4$) through the arrangement of tetrahedral and octahedral sheets. The distance between the silicate layers is 0.72 nm [24]. The cation exchange capacity and specific surface area values of lamellar kaolinite can be significantly increased by exfoliation. To create a novel class of materials with enormous promise as super absorbents, drug delivery systems, tissue scaffolds, rheological modifiers, wound dressings, and biosensors, exfoliated kaolinite nanosheets can be combined with polymer to form nanocomposites.

The methods used for the synthesis of clay–polymer hybrid composites, the mechanism involved during the synthesis, the physicochemical properties of the composites prepared using different polymer matrices, and finally the application of these clay–polymer composites in removal of dye and heavy pollutants from waste water are discussed below.

3 Methods of Synthesis

Clay–polymer hybrid composites can be classified on the basis of method of synthesis. Figure 4 outlines the general methods of synthesis of nanocomposites.

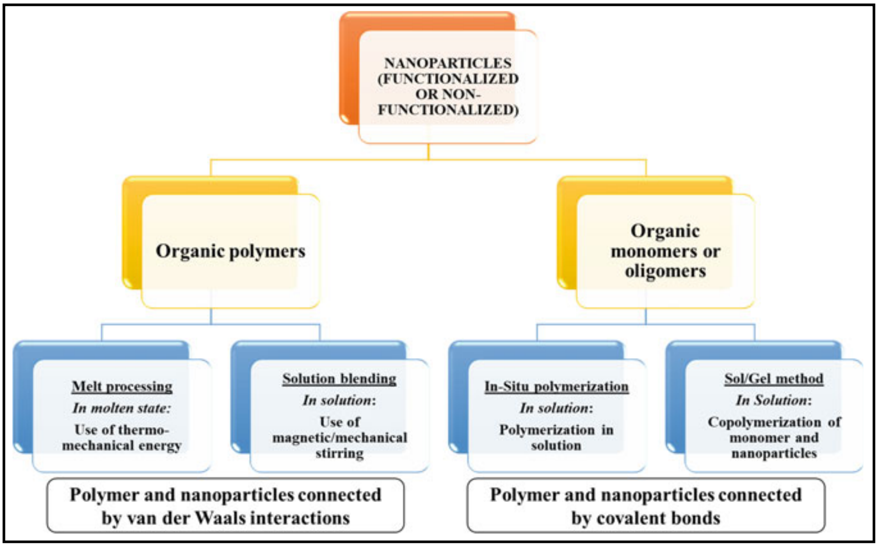


Fig. 4 Outline of the techniques used in the preparation of nanocomposites [2]

3.1 In Situ Polymerization Method

This method is mostly used to obtain well exfoliated clay platelets in the polymer matrix [9]. In this method, an initiation step takes place which results in the development of a hybrid between the polymer molecules and the organoclay. The organo-modified clay is swelled within a liquid monomer solution, which ultimately leads to the monomer dispersion in between the clay spacing. Thereafter, the polymerization process takes place to form the polymer. The polymerization step can be triggered by applying radiation or thermal energy along with a catalyst or an initiator which is added prior hand before the clay layers get expanded by ion exchange method [2]. The in situ polymerization method (i) tolerates resourceful molecular strategies of the polymer matrix, (ii) is an effective approach for the synthesis of polymer nanocomposites having extended property range, and (iii) is a technique which helps in developing an interface between the filler and the polymer matrix by modifying the matrix structure and its composition as well. This technique is generally used for formation of composite with thermosetting polymers.

3.2 Solution Blending Method

This technique is one of the easiest methods amongst the three methods available. This technique is also called solution-induced intercalation. The polymer is dissolved in a solvent initially along with clay dissolved in the same solvent separately. The clay solution is then poured in the polymer solution and homogenized for a uniform amount of time followed by evaporation of solvent [2]. However, use of organic solvents makes the method environmentally unsafe [25]. The major driving force in the intercalation process in this technique is the increase in total disorderliness of the system which is also called as desorption process of the solvent molecules. Solution blending method gives rise to uniform nanoclay dispersion.

3.3 Melt Blending Method

The melt blending technique is an industrially viable method which is eco-friendly and has high economic potential [1]. This method provides a better compatibility between the clay and the polymer as the polymer is directly reinforced in the polymer matrix. The mixture is then annealed over the polymer's melting point [2]. The melt-mixing generally results in three different polymer–clay morphologies. When the polymer is not able to diffuse in the interlayer spacing and the clay instead of getting dispersed stays in an agglomerate state, microcomposites are obtained. The intercalated nanocomposite is obtained when the multilayer morphology is seen with the polymer chains diffuse into the interlayer and the spacing is approximately

2–4 nm [10]. The third type of morphology obtained is exfoliated one where the individual clay platelets get suspended in a polymer melt with the interlayer distance of 8–10 nm [10]. The most preferred is exfoliated morphology which gives the largest matrix-filler contact area. The melt intercalation method provides an advantage that the technique is very specific as there is intercalation in systems where solvent is not involved. This technique is widely used for the fabrication of poly lactic acid/clay nanocomposites [25].

3.4 Sol–Gel Method

The technique involves dissolving the desired oligomer or polymer in sol–gel solution followed by hydrolysis and condensation of clay. The polymer involved in the composite can be cross-linked for better interaction with clay. Cross-linking by organo-functional silanes is widely adopted wherein the organo silyl groups can be hydrolyzed and co-condensed to form clay–polymer composite. Cross-linking leads to an improvement in thermal stability, resistance to solvents, and deformation.

Dual layer nanocomposite can be formed by sol–gel technique [26]. The advantage of this method is that a more uniform and well-oriented material is obtained. The surface area of the material is also high and nano-sized particles can be achieved with ease. The processing temperature here is low which results in homogeneity and the reaction can be controlled stoichiometrically to render pure products. The technique yields product which has high strength and high specific modulus [27].

Other types of modification include the formation of clay–polymer magnetic composites wherein the polymer matrix is filled with magnetic clay nanoparticles. Even clay–biopolymer nanocomposites have been formed to improve the properties such as surface functionality and reactivity. One of the best examples for this is the composite formed from chitosan which have proven to be excellent adsorbents for the removal of pollutants from water [28].

4 Characterization of Clay–Polymer Nanocomposites

Various techniques have been employed to characterize the composites. Techniques like Fourier transform infrared spectroscopy, scanning electron microscopy, field emission scanning electron microscopy, X-ray diffraction, Brunauer–Emmett–Teller (BET) analysis, UV–Vis spectroscopy, and high-resolution transmission electron microscopy (HRTEM) have been used [11].

XRD and TEM are two complementary techniques to analyse the structure of nanocomposites [2]. XRD is a useful technique for the determination of the interlayer space between layered silicates and the changes in the interlayer space during the formation of a nanocomposite. A decrease in the 2θ value that is the increase in d-value, due to expansion is indicative of formation of intercalated structures. This expansion gives us an understanding that the polymer has penetrated the separation but there is preservation of the repeated layer structure. The structure of the silicate is unaffected in phase-separated polymer-organoclay mixes so the organoclay basal reflection remains the same. The exfoliated structures have a lot of layer separation due to which the layer stacking is interrupted, and hence, there are no observable peaks. This disappearance of the peaks is due to extreme separation or due to the lack of the order in the nanocomposite. However, XRD has some limitations, as it is imperfect for measuring delaminated and exfoliated polymer–clay nanocomposites as no peaks are visible in this case [2]. The degree of crystallinity offered by polymers and their composites impacts the application of that composite [14]. Exfoliation means disorderliness which sometimes also leads to amorphous peaks [6].

XRD of pure montmorillonite (the most common clay used for the formation of polymer–clay nanocomposites) can be seen at $2\theta = 7$, 14, 19 and 26^0. And according to Scherer equation, the nano-montmorillonite shows crystallite size of 38.4 nm [15]. The peak of SiO_2 emerges at $2\theta = 26.96^0$, whereas the peak at $2\theta = 20.12^0$ is attributed to the aluminium silicate (Al_2SiO_5) [29]. Similarly, the kaolinite peak is seen at $2\theta = 9.58^0$ and 29.06^0 which shows some amount of crystallinity [30].

TEM provides better information about the structure and gives elaborate information about the morphology and defects present on the surface. The TEM images enable us to recognize the heavy atoms such as Al, Si, and O of the clay as well as the lighter atoms like C and H of the polymer. Even the filler atoms such as Na and Mg can be seen in the TEM images. The dark lines in TEM represent the layered silicates and the polymer appear brighter. So, this spacing between the dark and the bright lines gives the idea between the intercalation and the way the clay has been dispersed in the polymer [2]. For example, a well-known and common composite is between montmorillonite (MMT) and polyaniline (PANI), which has been well characterized using low angle XRD from an angle of 3^0 to 70^0. Polyaniline exhibits s peaks at about $2\theta = 15^0$, 20^0, and 25^0 while the MT used to synthesize the composite showed a typical peak at $2\theta = 6.08\ ^0$, which corresponded to a d-spacing of 14.52 Å. If the peaks are sharp, it indicated crystallinity of the polymer [30].

Similarly, SEM images also help in knowing the structures of the composites. For example, a biopolymer–clay nanocomposite derived from biopolymer of *M. olifera* seed showed SEM images where a rough profile was obtained due to the insertion of biopolymer in between the layers of the clay structures. It showed that the biopolymer was well seated in the clay layers and the exfoliation of the polymer achieved was good. The SEM images thus helped in identification of the nanostructure composite formed in between the clay and polymer layers [14]. The signal intensity at each pixel usually corresponds to a number which is proportional to the number of electrons that are emitted from the surface and is represented as a greyscale value. Usually, as reported previously it has been seen that the fillers in general have been identified and characterized as white bands (upper grey values) while the polymer matrix can be identified as black bands (lower grey values) [10].

In case of FTIR, the pure components and the nanocomposites can be distinguished by the vibrational spectral bands obtained before and after nanocomposite formation. For example, in the polyaniline montmorillonite composite the typical

Si–O bands have been identified at 1016 and 1101 cm^{-1} which also were present in the individual components confirming the intercalation of the two components. FTIR helps to distinguish between the pure clay and the organo-modified clay too. MMT and the organo-MMT is one such example. The peaks obtained at 3600–3000 cm^{-1} were attributed to the OH and NH stretching which were obtained as broad peaks in the organo-modified MMT. The Si–O in-plane stretching was found in the range of 1003–1087 cm^{-1} which after the formation of the organically modified MMT shifted to lower energy by 10–12 cm^{-1} [6].

The Karaya gum-graft-poly (2-methacryloloxy ethyl) trimethyl ammonium chloride/montmorillonite clay composite (KG-g-PMETAC/MMT) is another example where FTIR has been used to characterize the functional groups present in the composite. Here, the band at 1727 cm^{-1} has been attributed to the $C = O$ stretching vibration, and the band at 1447 cm^{-1} is given to the bending vibration of quaternary ammonium groups present in the matrix. The bands at 1030 cm^{-1}, 910 cm^{-1}, and 852 cm^{-1} have been attributed to the presence of Si–O in-plane stretching, Al-O and Mg-O bending vibrations of the clay [31].

Techniques based on X-ray spectroscopy such as X-ray photoelectron spectroscopy, energy-dispersive X-ray spectroscopy, and near edge X-ray absorption fine structure spectroscopic techniques help in understanding the chemical compositions of the clay–polymer nanocomposites materials. Usually, the elements of interest in organic polymer nanocomposites that can be identified by XPS are C(1 s) at 285 eV, N(1 s) at 398 eV, O(1 s) at 531 eV, F(1 s) at 685 eV, Si(2p) at 99 eV, S(2p) at 164 eV, S(2 s) at 228 eV, P(2p) at 130 eV, P(2 s) at 188 eV, Cl(2p) at 200 eV, Cl(2 s) at 271 eV, and Br(3d) at 69 eV binding energies.

The carbon-based bonds as well as the main chain elements can be characterized by XPS. A more effective method which gives us more surface-sensitive information is angle-resolved XPS. Here, the detection limits are considerably reducing and the XPS signal from an area closer to the surface is obtained. If the thickness of the polymer film is less than 3λ, then the non-destructive vertical chemical composition and the distribution of the elements can also be analysed.

Energy Dispersive X-ray Spectroscopy is another widely used non-destructive technique for both qualitative and quantitative analysis. Here, the energy of the emitted X-rays is characteristic of the types of elements present in the material. This technique when combined with SEM helps us to closely examine the chemical composition of the three-dimensional structure.

Another emerging technique is the X-ray Absorption Spectroscopy which involves the near-edge absorption fine structure (NEXAFS) The edge where the X-ray is absorbed by the target is characteristic of the element in the sample as the signal is generated by the resonance of the electron waves and the backscattered electron waves of the other electrons surrounding the atom. K-edge spectrum of the carbon is examined when it comes to identification of C(1 s) electron in organic/polymeric materials and composites. The techniques provide both quantitative and qualitative analysis giving us an idea of orientation and composition of the material [32].

The thermal stability of the composite can be analysed by thermogravimetric analysis (TGA). The volatile matter that is liberated as the composite degrades as a function of temperature is studied. The addition of clay in the polymer matrix adds to thermal stability. The TGA weight loss stages are generally divided into three main steps (a) the loss of water content, hydroxyl groups, and volatile compounds of the polymer, (b) decomposition of aliphatic chains and dehydration of the cellulosic rings or other components present, and (c) degradation of matrix remaining if any [15]. One of the examples for this is PMMA-MMT nanocomposites which has 40–50 ^{0}C greater decomposition temperature than the individual components [2]. Another example is the comparison of pure polystyrene (PS) and polystyrene nanoclay composite which again shows a 30–40 ^{0}C stability over the pure polystyrene.

The tensile properties can also be analysed. It is generally seen that the tensile strength in organically modified polymers increased with increase in clay content from 0 to 6 wt %, but the increase then ceased beyond 6 wt% and instead a decrease was found. The addition of organoclay increases the tensile strength and is due to the agglomeration of the organo-clay particles and intercalation between the organoclay and the polymer matrix [6]. The organically modified sodium montmorillonite by octadecyl ammonium-zinc oxide nanoparticles which has been incorporated in the chitosan matrix and used for food packaging has also exhibited similar behaviour [31].

BET analysis gives an idea about the surface area and the pore size of the polymer. For example, in the MMT/PANI composite [33], the PANI showed a porous morphology, whereas the MMT clay had a less porous morphology and therefore had a lesser specific surface area. The formed composite had a lesser surface area than pure PANI possibly due to the intercalation; however, the adsorption properties were found to be better than the pure PANI.

5 Application

Contamination and degradation of the aquatic environment are the major global concern of our society. The limitation of clean drinking water sources urges a necessity to either treat the waste before discarding it to the water bodies or treat the polluted water in rivers, lakes, and other aquatic bodies. A lot of industrial effluent including organic and inorganic wastes, heavy metals, dyes, and aromatic compounds is discharged in the water bodies untreated which pose a considerable risk to the clean drinking water sources. These are harmful to both humans and aquatic life in the water bodies. Thus, the removal of these pollutants is absolute necessity. Clay–polymer composites act as efficient adsorbents in the uptake of these pollutants and treatment of the water bodies.

With the growth of textile industries, the pollution of water bodies with the untreated discharged dyes is increasing. Dyes usually are synthetic in origin, have complex aromatic molecular structures which are more stable and difficult to biodegrade. They can be cancerous and mutagenic to humans. They also prevent the penetration of light from the surface of water thus hampering the photosynthesis process of aquatic life.

Heavy metals contained in industrial effluents constitute a major environmental concern as they are persistent, cannot be degraded/destroyed, and can be biomagnified by organisms. Presence of these metals above the permissible limits in drinking water can alter the metabolic body processes and induces impairment and dysfunction in blood and cardiovascular system in human adults and particularly in children.

The removal of these heavy metals and dyes using adsorption by clay–polymer nanocomposites remains an interesting area of research. Table 2 shows the recent application of clay–polymer hybrid composites in the removal/uptake of dyes and heavy metals.

The adsorption efficiency of dyes and heavy metals can be attributed to the electrostatic attraction between the pollutant and the adsorbent. The various interactions between the surface functional groups of the clay–polymer hybrid composite and the dye/heavy metal leads its adsorption on the surface of the adsorbent. For instance, Chitosan-Glyoxal/Kaolin used for the removal of Remazol Brilliant Blue R (at pH 4) has -NH_2, -OH and Si–OH groups on the surface. At the acidic pH value, the amino group as -NH_3^+ along with the positively charged surface of the composite material resulted in electrostatic attraction of the sulfonic acid groups of the dye. Hydrogen bonding and n-π interactions between the clay composite and the aromatic ring of the dye further augment the adsorption process [32]. The electrostatic interactions and hydrogen bonding between adsorbent and adsorbate were confirmed from FTIR and XPS analysis. The appearance of characteristic peaks of functional groups of adsorbates in FTIR of composite and the shifts observed in XPS proved the interaction between them [11]. The interaction between Methyl Orange and clay–polymer composite were discussed on similar grounds by Kang et.al. [35]. Quin et al. discussed the interaction between Cu^{2+} and the clay composite based on the appearance of Cu^{2+} peak in XPS after adsorption and disappearance of the peak of sodium due to cation exchange between sodium ions and copper ions [36].

Thus, electrostatic interaction between the surface of the clay–polymer hybrid composite and the dye/heavy metal plays a role in the removal of the pollutant. Also, hydrogen bonding between the surface functional groups and those of the adsorbate contribute to the removal. If the molecular structure of the pollutant has the presence of aromatic rings, then n-π interactions also contribute to the adsorption phenomenon.

6 Conclusion

This book chapter provides a comprehensive overview on the properties of clay–polymer hybrid composites, different polymers used for the surface modification which contribute to an enhancement in various physicochemical properties of clay, various methods of synthesis and finally the environmental applications of clay–polymer hybrid composites focussing on the adsorption of dyes and removal of heavy metals. The intercalated clay/polymer composites show high mechanical

Table 2 Recent application of clay–polymer hybrid composites in the removal/uptake of dyes and heavy metals

Adsorbent	Adsorbate	pH	Removal efficiency (%) or Adsorption capacity (mg/g)	Isotherm model	Kinetic model	Ref
Polyaniline/ Montmorillonite clay nanocomposites	Green 25	6	100%	Langmuir	Pseudo Second order	30
Montmorillonite nanosheet/poly (acrylamide-co-acrylic acid)/sodium alginate hydrogel beads	Methylene blue	6.83	530.7 mg/g	Freundlich	Pseudo Second order	11
Polyacrylate/Bentonite	Pb (II)	–	1554 mg/g	Langmuir	Pseudo Second order	34
Chitosan/Montmorillonite	Methyl Orange in presence of Methylene Blue	3	1060 mg/g	Langmuir	Pseudo First order	35
Chitosan hydrogels/ Montmorillonite nanosheets	Cu (II)	4	119.42 mg/g	Langmuir	Pseudo Second order	36
Chitosan/Montmorillonite	Methylene Blue	8	276.03 mg/g	Freundlich, Dubinin-Radushkevish	Pseudo Second order	14
Chitosan/ Montmorillonite/ Polyaniline	Methylene Blue	–	111 mg/g	Temkin	Pseudo Second order	37
Polypropylene-g-Maleic Anhydride-Chitosan/ Montmorillonite	Pb (II)	8	90.9%	Langmuir	Pseudo Second order	38
Chitosan/Polyacrylic acid/ bentonite	Malachite Green	6	454.55 mg/g	Langmuir	Pseudo Second order	39
Cross-linked Chitosan/ Bentonite beads	Crystal Violet	5	169.49 mg/g	Langmuir	Pseudo Second order	40
Chitosan-Glyoxal/Kaolin	Remazol Brilliant Blue R	4	447.1 mg/g	Langmuir and Freundlich	Pseudo Second order	32

(continued)

Table 2 (continued)

Adsorbent	Adsorbate	pH	Removal efficiency (%) or Adsorption capacity (mg/g)	Isotherm model	Kinetic model	Ref
Chitosan-Azadirachta indica/Kaolinite	Congo Red, Methylene Blue	6,7	104.66 mg/g, 99.01 mg/g	Langmuir	Pseudo Second order	29
Cellulose/Clay composite	Rhodamine B	2	95.6%	Redlich-Peterson	Pseudo Second order	15
Cellulose/Clay bio composites	Pb (II), Cd (II)	7	265.67 mg/g, 50.38 mg/g	Langmuir	Pseudo Second order	41
Carboxymethyl/Chitosan/Montmorillonite	Pb (II), Congo Red	5,7	87.95 mg/g, 91.77 mg/g	Langmuir	Pseudo Second order	42
Carboxymethyl cellulose-g poly (acrylamide)/montmorillonite nanocomposite	Malachite Green	7	172.4 mg/g	Langmuir	Pseudo Second order	43
Zr (IV) encapsulated carboxymethyl cellulose/montmorillonite	Reactive Red 2, Acid Orange 7	3	100%	Freundlich	–	44
Graphene oxide-montmorillonite/sodium alginate aerogel beads	Methylene Blue	5.99	150.66 mg/g	Freundlich	Pseudo Second order	45
Karaya gum-graft-poly (2-methacryloyloxy ethyl) trimethyl ammonium chloride/montmorillonite clay composite	Methylene Blue, Toluidine Blue, Crystal Violet, Azure B	–	155.85 mg/g, 149.64 mg/g, 137.77 mg/g, 128.78 mg/g	Freundlich	Pseudo First order	46
Tetraethoxysilane functionalized Na-bentonite polysulfone/polyethylenimine composites	Methylene Blue	–	99%	–	–	47

(continued)

Table 2 (continued)

Adsorbent	Adsorbate	pH	Removal efficiency (%) or Adsorption capacity (mg/g)	Isotherm model	Kinetic model	Ref
M. Oleifera/Bentonite	Cd (II), Cr (VI), Pb (II)	6–8, 2–4, 5–7	99.99%	Langmuir, Langmuir, Freundlich	–	14

strength, filler volume, tensile strength, and thermal properties which are beneficial from the point of view of environmental application of pollutants and remediation of waste water. Though the low cost and readily available clay minerals have been considered as adsorbents of choice, their practical use as adsorbents is limited due to their low adsorption tendency towards organic species, difficulty in regeneration and recovery. Clay-polymer composites combining the advantageous characteristics of clay minerals and polymers have emerged as attractive alternative with high adsorption efficiency, surface area and renderability. The different classes of polymers that have been used in formation of composites include chitosan, polystyrene, polypropylene, polyesters, polyurethanes, epoxies, and polyvinyl chloride. The synthesized composites are known to exhibit enhancement in the adsorption potential for effective removal of the pollutants. Methods such as in situ polymerization, solution-induced intercalation, and melt processing have been described in detail. The unique characteristics and properties of the synthesized material using the above techniques have been noted and described in brief. Various characterization techniques applied allows us to distinguish between intercalated, exfoliated, and phase-separated polymer clay nanocomposites. Through the tensile property studies, one can conclude the tensile strength especially in organically modified materials and increase with the percentage load of the clay up to 6% of weight after which a decrease in the tensile strength was seen. The later part of the chapter highlights the application of the clay composites in the environmental area such as removal/uptake of dyes and heavy metals from water resources. Hence, clay–polymer hybrid nanocomposites are highly promising material for waste water treatment along with robust and rugged material property for environmental application is now prominent for sustainable future.

References

1. Mohapi, M., Sefadi, J.S., Mochane, M.J., Magagula, S.I., Lebelo, K.: Effect of LDHs and other clays on polymer composite in adsorptive removal of contaminants: A review. Crystals **10**(11), 1–39 (2020). https://doi.org/10.3390/cryst10110957
2. Dalia, E., Abulyazied, A. E.: An investigative study on the progress of nanoclay-reinforced polymers: preparation, properties, and applications: a review. Polymers (Basel), (13), 4401(2021). https://doi.org/10.3390/polym13244401
3. Access, O.: We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists TOP 1%. https://doi.org/10.5772/intechopen.92529
4. Barakan, S., Aghazadeh, V.: The advantages of clay mineral modification methods for enhancing adsorption efficiency in wastewater treatment : a review. (2020). https://doi.org/10.1007/s11356-020-10985-9
5. Khodakarami, M., Bagheri, M.: Recent advances in synthesis and application of polymer nanocomposites for water and wastewater treatment. J. Clean. Prod. **296**, 126404 (2021). https://doi.org/10.1016/j.jclepro.2021.126404
6. Sudhakar, Y.N., Selvakumar, M., Krishna Bhat, D.: Investigation on thermos-mechanical properties of organically modified polymer clay nanocomposites for packaging application. Polym. Polym. Compos. 1–9(2020). https://doi.org/10.1177/0967391120960645
7. Rehman, S.U., Javaid, S., Shahid, M., Gul, I.H., Rashid, B., Szczepanski, C.R., Naveed, M., Curley, S.J.: Polystyrene-sepiolite clay nanocomposites with enhanced mechanical and thermal properties. Polymers **14**(17), 3576 (2022). https://doi.org/10.3390/polym14173576
8. Merzah, Z.F., Fakhry, S., Allami, T.G., Yuhana, N.Y., Alamiery, A.: Enhancement of the properties of hybridizing epoxy and nanoclay for mechanical, industrial, and biomedical applications. Polym. **14**(3), (2022). https://doi.org/10.3390/polym14030526
9. Sen, M.: Nanocomposite materials. In: Sen. M. (ed.) Nanotechnology and the environment. IntechOpen, London (2020). https://doi.org/10.5772/intechopen.93047
10. Stojšić, J., Raos, P., Milinović, A., Damjanović, D.: A study of the flexural properties of PA12/Clay nanocomposites. Polym. **14**(3), (2022). https://doi.org/10.3390/polym14030434
11. Wang, W. et al.: Efficient dye removal using fixed-bed process based on porous montmorillonite nanosheet/poly (acrylamide-co-acrylic acid)/sodium alginate hydrogel beads Applied Clay Science Efficient dye removal using fixed-bed process based on porous montmorillonite nanosheet/poly (acrylamide-co-acrylic acid)/sodium alginate hydrogel beads. Appl. Clay Sci. **219**, 106443 (2022). https://doi.org/10.1016/j.clay.2022.106443
12. Berber, M.R.: Current advances of polymer composites for water treatment and desalination. J. Chem. **2020**, (2020). https://doi.org/10.1155/2020/7608423
13. Amari, A. et al.: Clay-polymer nanocomposites: preparation and utilization for pollutants removal. pp. 1–21 (2021). https://doi.org/10.3390/ma14061365
14. Ravikumar, K., Udayakumar, J.: Preparation and characterisation of green clay-polymer nanocomposite for heavy metals removal. Chem. Ecol. (2020). https://doi.org/10.1080/02757540.2020.1723559
15. Kausar, A., Shahzad, R., Asim, S., Bibi, S., Iqbal, J., Muhammad, N.: Experimental and theoretical studies of Rhodamine B direct dye sorption onto clay-cellulose composite. J. Mol. Liq. **328**, 115165 (2021). https://doi.org/10.1016/j.molliq.2020.115165
16. Orta, M. et al.: Applied clay science biopolymer-clay nanocomposites as novel and ecofriendly adsorbents for environmental remediation. Appl. Clay Sci. **198**, 105838 (2020). https://doi.org/10.1016/j.clay.2020.105838
17. Xu, D., Wang, S., Berglund, L.A., Zhou, Q.: Surface charges control the structure and properties of layered nanocomposite of cellulose nano fibrils and clay platelets. (2021). https://doi.org/10.1021/acsami.0c18594
18. Junior, C.R.F., Fernandes, R.S., De Moura, M.R., Aouada, F.A.: On the preparation and physicochemical properties of pH-responsive hydrogel nanocomposite based on poly (acid methacrylic)/laponite RDS. Mater. Today Commun. **23**, 100936 (2020). https://doi.org/10.1016/j.mtcomm.2020.100936

19. Iqbal, Z., Habib, U.,.;, Binti, Z. Mechanical and thermal properties of sepiolite strengthened thermoplastic polymer nanocomposites : A comprehensive review. Alexandria Eng. J. (2021). https://doi.org/10.1016/j.aej.2021.06.015. https://doi.org/10.1016/j.aej.2021.06.015
20. Khan, Z. I., Mohamad, Z. B.: A novel recycled polyethylene terephthalate/polyamide 11 (rPET / PA11) thermoplastic blend (2021). https://doi.org/10.1177/14777606211001074
21. Asensio, M., Herrero, M., Núñez, K., Merino, J. C., Pastor, J. M.: The Influence of sepiolite orientation and concentration, on the morphological, thermal and mechanical properties of bio-polyamide 4. 10 Nanocomposites. pp. 1–9 (2020). https://doi.org/10.1002/pen.25359
22. Shuai, M. A. et al.: Nanocomposite polymer hydrogels reinforced by carbon dots and hectorite clay. pp 287–292 (2020). https://doi.org/10.1007/s11595-020-2255-z
23. Sapalidis, A.A., Katsaros, F.K., Steriotis, T.A., Kanellopoulos, N.K.: Properties of poly (vinyl alcohol)— bentonite clay nanocomposite films in relation to polymer—Clay interactions (2011). https://doi.org/10.1002/app.34651
24. Costa, J. et al.: Kaolinite review : intercalation and production of polymer nanocomposites. pp. 28–44 (2022). https://dx.doi.org/10.30919/es8d499
25. Singha, S., Hedenqvist, M.S.: A review on Barrier Properties of Poly(Lactic Acid)/Clay Nanocomposites. Polymers **12**, 1095 (2020). https://doi.org/10.3390/polym12051095
26. Omanović-Mikličanin, E., Badnjević, A., Kazlagić, A., Hajlovac, M.: Nanocomposites: a brief review. Heal. Technol. (2019). https://doi.org/10.1007/s12553-019-00380-x
27. Hafeez, M.: Recent progress and overview of nanocomposites. In: Sharma, A. (ed.), Nanocomposite materials for biomedical and energy storage applications. Intech Open, London (2022). https://doi.org/10.5772/intechopen.102469.
28. El-Kousy, S.M., El-Shorbagy, H.G., El-Ghaffar, M.A.A.: Chitosan/montmorillonite composites for fast removal of methylene blue from aqueous solutions. Mater. Chem. Phys. **254**, 123236 (2020). https://doi.org/10.1016/j.matchemphys.2020.123236
29. Ahmad, R., Ansari, K.: Comparative study for adsorption of congo red and methylene blue dye on chitosan modified hybrid nanocomposite. Process Biochem. **108**(May), 90–102 (2021). https://doi.org/10.1016/j.procbio.2021.05.013
30. Kalotra, S., Mehta, R.: Synthesis of polyaniline/clay nanocomposites by in situ polymerization and its application for the removal of Acid Green 25 dye from wastewater. Polym. Bull. **78**(5), 2439–2463 (2021). https://doi.org/10.1007/s00289-020-03222-3
31. Son, D., Cho, S., Nam, J., Lee, H., Kim, M.: X-ray-based spectroscopic techniques for characterization of polymer nanocomposite materials at a molecular level. Polymers **12**, 1053 (2020). https://doi.org/10.3390/polym12051053
32. Jawad, A.H.: Composite: Parametric optimization for Color removal and COD reduction of remazol brilliant blue R dye. J. Polym. Environ. **30**, 168–174 (2021). https://doi.org/10.1007/s10924-021-02188-1
33. Maria, T.C., Giuseppe, M., Letterio, M., et al.: Self-assembly processes in hydrated montmorillonite by FTIR investigations. Materials **13**, 1100 (2020)
34. Chen, Y., gui, Liao, R. ping, Yu, C., Yu, X.: Sorption of Pb (II) on sodium polyacrylate modified bentonite. Adv. Powder Technol. **31**(8), 3274–3286 (2020). https://doi.org/10.1016/j.apt.2020.06.011
35. Kang, S., Qin, L., Zhao, Y., Wang, W., Zhang, T.: Chemosphere enhanced removal of methyl orange on exfoliated montmorillonite/chitosan gel in presence of methylene blue. Chemosphere **238**, 124693 (2020). https://doi.org/10.1016/j.chemosphere.2019.124693
36. Qin, L., Zhao, Y., Wang, L., Zhang, L., Kang, S.: Chemosphere Preparation of ion-imprinted montmorillonite nanosheets/chitosan gel beads for selective recovery of Cu (II) from wastewater. Chemosphere **252**, 126560 (2020). https://doi.org/10.1016/j.chemosphere.2020.126560
37. Minisy, I.M., Salahuddin, N.A., Ayad, M.M.: Applied clay science adsorption of methylene blue onto chitosan—montmorillonite/polyaniline nanocomposite. Appl. Clay Sci. **203**, 105993 (2021). https://doi.org/10.1016/j.clay.2021.105993

38. Moja, T.N., Bunekar, N., Mishra, S.B., Tsai, T.Y., Hwang, S.S., Mishra, A.K.: Melt processing of polypropylene-grafted-maleic anhydride/Chitosan polymer blend functionalized with montmorillonite for the removal of lead ions from aqueous solutions. Sci. Rep. **10**(1), 1–14 (2020). https://doi.org/10.1038/s41598-019-57079-2
39. Yildirim, A., Bulut, Y.: Adsorption behaviors of malachite green by using crosslinked chitosan/polyacrylic acid/bentonite composites with different ratios. Environ. Technol. Innov. **17**, 100560 (2020). https://doi.org/10.1016/j.eti.2019.100560
40. Vithalkar, S.H., Jugade, R.M.: Adsorptive removal of crystal violet from aqueous solution by cross-linked chitosan coated bentonite. Materials Today: Proceedings **29**, 1025–1032 (2020). https://doi.org/10.1016/j.matpr.2020.04.705
41. Abu-danso, E., Peräniemi, S., Leiviskä, T., Kim, T.: Synthesis of clay-cellulose biocomposite for the removal of toxic metal ions from aqueous medium. J. Hazard. Mater. **381**, 120871 (2020). https://doi.org/10.1016/j.jhazmat.2019.120871
42. Zhang, H., Ma, J., Wang, F., Chu, Y., Yang, L., Xia, M.: Mechanism of carboxymethyl chitosan hybrid montmorillonite and adsorption of Pb (II) and Congo red by CMC-MMT organic-inorganic hybrid composite. Int. J. Biol. Macromol. **149**, 1161–1169 (2020). https://doi.org/10.1016/j.ijbiomac.2020.01.201
43. Jamaleddin, S., Aghamohammadi-bavil, O., Foroutan, R., Arsalani, N.: Removal of malachite green using carboxymethyl cellulose- g - polyacrylamide/montmorillonite nanocomposite hydrogel. Int. J. Biol. Macromol. **159**, 1122–1131 (2020). https://doi.org/10.1016/j.ijbiomac.2020.05.093
44. Sirajudheen, P., Karthikeyan, P., Basheer, M.C., Meenakshi, S.: Adsorptive removal of anionic azo dyes from effluent water using Zr (IV) encapsulated carboxymethyl cellulose-montmorillonite composite. Environmental Chemistry and Ecotoxicology **2**, 73–82 (2020). https://doi.org/10.1016/j.enceco.2020.04.002
45. E, T., Ma, D., Yang, S., Hao, X.: Graphene oxide-montmorillonite/sodium alginate aerogel beads for selective adsorption of methylene blue in wastewater. J. Alloy. Compd. **832**, 154833 (2020). https://doi.org/10.1016/j.jallcom.2020.154833
46. Preetha, B.K., Vishalakshi, B.: Microwave assisted synthesis of karaya gum-based montmorillonite nanocomposite: Characterisation, swelling and dye adsorption studies. Int. J. Biol. Macromol. **154**, 739–750 (2020). https://doi.org/10.1016/j.ijbiomac.2020.03.107
47. Saki, S., Senol-Arslan, D., Uzal, N.: Fabrication and characterization of silane-functionalized Na-bentonite polysulfone/polyethylenimine nanocomposite membranes for dye removal. J. Appl. Polym. Sci. **137**(36), 1–12 (2020). https://doi.org/10.1002/app.49057

Environmental Applications

Clay Mineral Composites as Environmental Catalysts

S. M. Dassanayake, Udari Prasadini Perera, C. L. Jayawardena, and Endene Emmanuel

Abstract Clay mineral-based composites are increasingly employed as environmental catalysts owing to their accessibility, biocompatibility, nontoxicity, and durability. Natural clay minerals are phyllosilicates with a typical structure containing nanoscale parallel sheets of silicate tetrahedra. These unique layers and interlayers can be modified to build innovative catalytic composites based on clay minerals. This chapter revisits the contemporary studies on the engineering of clay-based composites, their fundamental physical and chemical properties, and their functional alterations, which have expanded the application of clay mineral composites as environmental catalysts. Furthermore, the chapter summarises the clay mineral composites' major environmental remediation applications from four perspectives: combustion catalysis, water treatment, biodiesel production, and photocatalysis. Alongside this, the potential of clay mineral composites as nanocatalysts is briefly discussed. Holistically, the chapter disseminates the foundation for new insights, problems, and prospects of clay mineral composites as environmental catalysts and their catalytic applications.

Keywords Clay minerals · Environmental catalysts · Composites · Nanocatalysts · Environmental catalysis

---

S. M. Dassanayake (✉)
Department of Decision Sciences, University of Moratuwa, Moratuwa, Sri Lanka
e-mail: sandund@uom.lk

U. P. Perera
Department of Chemical and Process Engineering, University of Moratuwa, Moratuwa, Sri Lanka

C. L. Jayawardena
Department of Earth Resources Engineering, University of Moratuwa, Moratuwa, Sri Lanka

E. Emmanuel
The World Bank, Washington, USA

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_16

1 Introduction

Expanding human civilization has produced several energy sources, materials, and chemicals to improve living conditions, primarily using resources mined from the earth. Consequently, multiple human activities emit many pollutants that harm air, land, and water sources. Moreover, the modern world faces an energy crisis due to the depletion of fossil fuel, coal, and gas supplies due to rising energy consumption and population expansion. As such, a dire need exists for renewable energy sources and robust environmental remediation technologies. To this end, low-cost clay-based minerals have gained a growing interest, given their effectiveness and profitability in producing novel catalysts, synthetic chemicals, composites, and fuels. Also, clay-based catalysts play a significant part in green chemistry due to their ability to reduce the usage and production of harmful compounds [1].

Clay minerals are a promising catalyst for purifying wastewater [2] and air [3]. Also, these catalysts can be effectively used in biodiesel production [4], hydrogen production [5], photocatalysis [6], and other environmental applications due to their abundance and low cost. In addition, they feature a large surface area, superior porosity, a high mechanical strength, and great thermal and chemical stability [7]. Similarly, the crystalline structure of clay minerals may be altered by various treatments to improve porosity and surface area and increase the number of active sites that facilitate the creation of intermediates between reactant and product [8]. To maximize the environmental advantages of catalysts, special consideration should be given to catalytic selectivity for the product, the catalyst's carbon footprint, waste output (amount of byproducts and inorganic compounds), catalyst loading and intrinsic activity, and catalyst recoverability [9].

Figure 1 shows a bibliometric analysis performed using search results of 136 research papers published from 2017 to 2023 in the Scopus database. From a broader perspective, the systematic review of these results highlights on replacing conventional acid, trace metal-based catalysts, and other inefficient catalysts with clay composite-based sustainable catalysts to improve the overall efficiency and eco-friendliness of the environmental process.

This chapter reviews the research on applying clay composites as environmental catalysts. The chapter opens with a brief overview and categorization of natural clay minerals. Also highlighted are the robust modification procedures utilised for these natural clay minerals. In this respect, the chapter seeks to establish a foundation for the broader scope of clay mineral composites and nanocomposites. The uses of clay minerals for environmental remediation are reviewed in four sections: combustion catalysis, water treatment, biodiesel synthesis, and photocatalysis. The review closes with a discussion of potential research opportunities and challenges in developing environmentally benign clay composite catalysts.

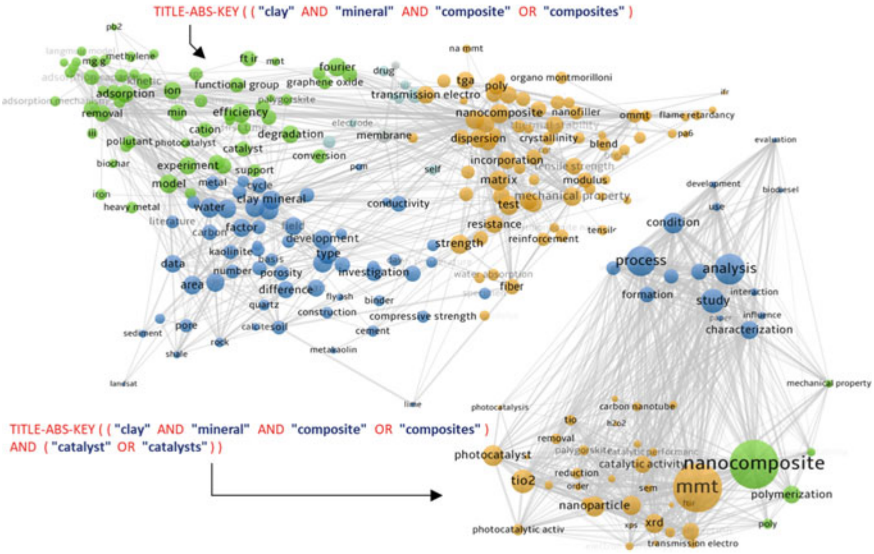


Fig. 1 Clay mineral and composites found in literature

2 Clay Minerals

Clay minerals are naturally occurring, inexpensive, layered aluminosilicates with desirable catalyst properties. These properties include smaller particle sizes, interlayer spacing that can be expanded, and cation exchangeability. Clay minerals have a sandwich-like structure comprising one or two layers of silicon oxide tetrahedral sheets adhered to an aluminium or magnesium octahedral sheet via electrostatic and hydrogen-bonding forces (Fig. 2). The kaolin group, which has a general composition of $Al_2Si_2O_5(OH)_5$, is formed when one tetrahedral sheet and one octahedral sheet bond. In contrast, phyllosilicates form when two tetrahedral sheets bond with one octahedral sheet. The thickness of kaolin group layers is approximately 0.7 nm, while the thickness of phyllosilicates is approximately 0.9 nm. Clay minerals with particle sizes less than 2 μm occur naturally in soils, sediments, and deposits. Abundant clay mineral types include kaolin, smectite [10], illite [11], and chlorite [12].

Naturally occurring clays, such as smectite, are negatively charged and welcome balancing cations in their interlayer space, whereas positively charged clays, such as chlorite, have counterbalancing anions. Clays have a porous structure that allows molecules to interact inherently, such as through adsorption, swelling, and ion exchange. As such, different types of clay facilitate various reactions. For instance, Montmorillonite (MMT) exhibits excellent adsorption capacity, high surface area, and interesting acidic properties, making it a successful catalyst in various reactions, including Friedel–Crafts alkylation, oxidative deprotection, and nucleophilic additions.

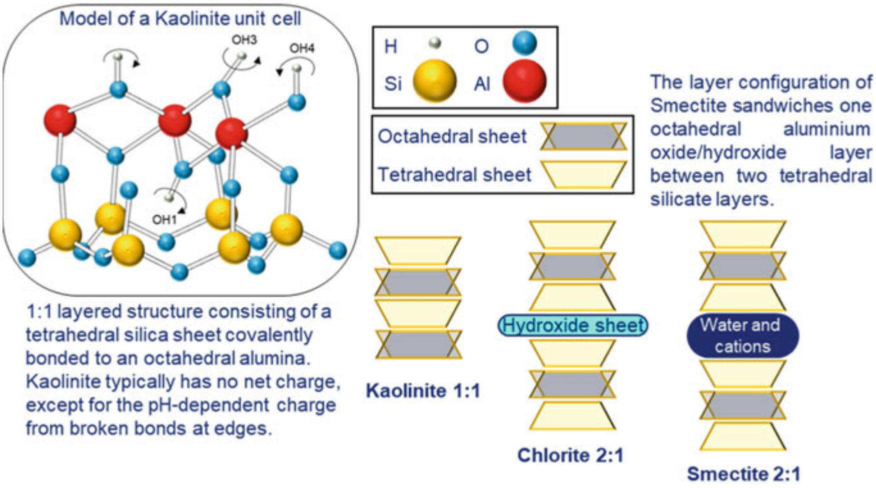


Fig. 2 Schematic structures of various clay minerals

2.1 Kaolinite

Kaolinite is a 1:1 layer hydrous alumino-silicate mineral [13] with generalized formula $Al_2O_3{\cdot}2SiO_2$. It is made by advance weathering of feldspar and other aluminosilicates, and it is one of the abundant minerals in soils and sediments. The structure of kaolinite has an alumina octahedral sheet and a silica tetrahedral sheet in an alternative fashion. The 1:1 layer is electrically neutral in kaolinite, and the layers are kept together by hydrogen bonding between the basal oxygens of the tetrahedral sheet and the hydroxyls of the outer plane of the adjacent octahedral sheet. Kaolinite contains 10–95% of kaolin along with mica and quartz and metal oxides including K_2O, CaO, TiO_2, Fe_2O_3, Na_2O, MgO, MnO, and P_2O_5 as impurities. Unmodified kaolinite has impurities, low porosity, and acidity that lower their catalytic ability [14]. Thus, clays should undergo pre-treatment such as thermal treatment, exfoliation, acid-leaching and pillaring before being utilised as catalyst supports. Kaolinite can be modified to suit many industrial uses such photocatalyst [15], catalyst supports [16] and modified catalysts [17] due to its abundance, mature mining technology and chemically modification ability. Various methods, including chemical activation, intercalation and thermal treatments are proposed in the literature to enhance Kaolinite catalytic activity. Modified Kaolinites' high stability, adsorption capacity, and high Lewis and Brønsted acid sites density which are desirable properties for catalysts. Kaolinite is commonly used as a precursor to synthesise Zeolite that has applications in variety of catalysis processes [18]. Halloysite is a 1:1 type kaolin group member with a multilayer nanotubular structure. The approximate physical dimensions of Halloysite range from 500 to 1000 nm in length and 100 to 200 nm in outer diameter with 15–20 nm channels/lumen in the tubes [19]. The general structural formula of Halloysite with one layer of water molecules in the interlayers is

$Al_2(OH)4Si_2O_5 \cdot H_2O$ [20]. This mineral can be functionalised at the nanoscale by exploiting supramolecular and covalent interactions. Once functionalised, halloysite nanotubes can be utilised as reinforcing fillers for polymers and vehicles carrying control release of active molecules, such as antioxidants, flame-retardants, corrosion inhibitors, biocides, and drugs. The self-assembling property of halloysite on the oil–water interface nanotubes makes them excellent substances for petroleum spill bioremediation and catalysis.

2.2 Smectite

Smectites (derived from the Greek word semcktos, meaning soap) are a group of highly absorbent clay minerals containing 2:1 layer hydroxyl aluminosilicate with a total negative layer charge of 0.2–0.6 per formula unit. Smectites are also called layered clay as they contain three layers composed of two tetrahedral sheets(contains Si^{4+} cations surrounded by four oxygen atoms) and one octahedral sheet in between [21]. The octahedral sheet contains divalent (i.e., Mg^{2+}) or trivalent (Al^{3+}) cations surrounded by six oxygen atoms. Different names are given to smectites based on the predominant octahedral cation, the location of isomorphic substitution, and whether the mineral is di- or trioctahedral. Dioctahedral smectites are the most common in soil, and the three major minerals include montmorillonite (MMT), beidellite, and nontronite. At the same time, saponite, sauconite, and hectorite are examples of trioctahedral smectites. Bentonite is a soft clay generated from alteration of volcanic ash and mainly consists of smectic minerals, especially MMT. MMT is a hydrated 2:1-layered dioctahedral aluminosilicate with a CEC of 70–130 meq per 100 g. MMT also has high swelling properties for adequate intercalation and intersalation (accommodation of ion-pair salt into the interlayer space). Kaolinite has lower cation exchangeability than MMT due to the low surface area. MMT consists of two-dimensional layers (thickness ~0.96 nm) formed by two Si–O tetrahedral sheets linked with an edge-shared octahedral sheet of either Al–O or Mg–O [22]. The formation of biopolymers, and the efficient support of MMT as heterogeneous catalysts, and the ability to develop solid acid catalysts have made it highly attractive to study. The expansive properties of the aluminosilicate layers of natural MMT protect the metal particles from leaching. Hence, the natural MMT holds arbitrary impurities (Fe^{2+}, Mn^{2+}) that hinder their catalytic performances.

Other smectite minerals such as hectorite, sapnolite, beidelite, and nontronite also contain in bentonite in small quantities. The chemical composition of bentonite highly varies with the mineralization environment and their catalytic ability varies as a result [23]. Various transition metal cations and alkali metal cations can be introduced to the octahedral sheet and the interlayer, respectively, and tune the acidic and basic properties of smectites to suit their catalyst activity. Smectite has a smaller particle size than most clays, hence owning a great surface area ranging from 650 to 800 m^2/g. The interlayer expansion of smectites promotes ion exchange, and smectites have a high cation exchange capacity (CEC) since they have a high concentration of interlayer cations. The surface properties, high CEC and acidity make Smectites a viable catalyst for many reactions [22, 24, 25].

2.3 Sepiolite

Sepiolite is a phyllosilicate mineral with a structural formula of $Mg_8Si_{12}O_{30}(OH)_4 \cdot 8[(H_2O)_4]$. It is a fibrous material with fine microporous channels with dimensions of 0.37 × 1.06 nm running parallel to the fibres' length, contributing to its high specific surface area. Sepiolite comprises ribbons with a 2:1 layered structure resulting from the inversion of SiO4 tetrahedra along a set of SiO sheets. This mineral has a discontinuous octahedral magnesium sheet, creating a net negative charge of about 0.2. A small number of exchangeable cations and coordinated water molecules along the channels balances the excessive negative charge. Natural sepiolite has a cation exchange capacity (CEC) of approximately 10 meq/100 g. However, various ionic and catalytic substitutions warrant sepiolite with different adsorption capacities of heavy metal cations with different CEC values. The adsorption capacity of heavy metals on sepiolite has been reported to follow the order of Cr(III) > Cd(II) > Cu(II) > Zn(II) > Ni(II) > Ag(I). This is inconsistent with the hydration of heavy metal cations because Si–OH and Mg^{2+} substitution in the sepiolite structure also affect the adsorption of heavy metal cations [23].

The high surface area and physiochemical activity make sepiolite effective at removing heavy metals and dyes. Also, these characteristics furnish sepiolite with more sites for catalytic activity and prevent nano-catalysts from aggregating. The unique structure and morphology of sepiolite increase catalysts' recyclability and flexibility when loaded on sepiolite [26]. As a result, sepiolite has been utilized as an adsorbent for cationic and anionic dyes such as methylene blue, acid red, and crystal violet and as a support and binder for metal oxide composites [23].

3 Clay Mineral Modifications

Modified clay catalysts show improved results compared to their original counterparts [27]. Therefore, different approaches have been utilized to alter the crystalline structure and optimize the active sites that help intermediate formation between reactant and product in a controlled way [8]. Four main modification methods can be highlighted for clay mineral modifications: thermal treatment, acid leaching, exfoliation, and pillaring (Fig. 3). Thermal treatment (dehydroxilation) refers to heating the clay minerals to extreme temperatures to remove hydroxyl groups. Exfoliation is the process of increasing the separation between the layers from their normal distance of 1 nm to about 20 nm or higher. To this end, the layers are disrupted and spatially

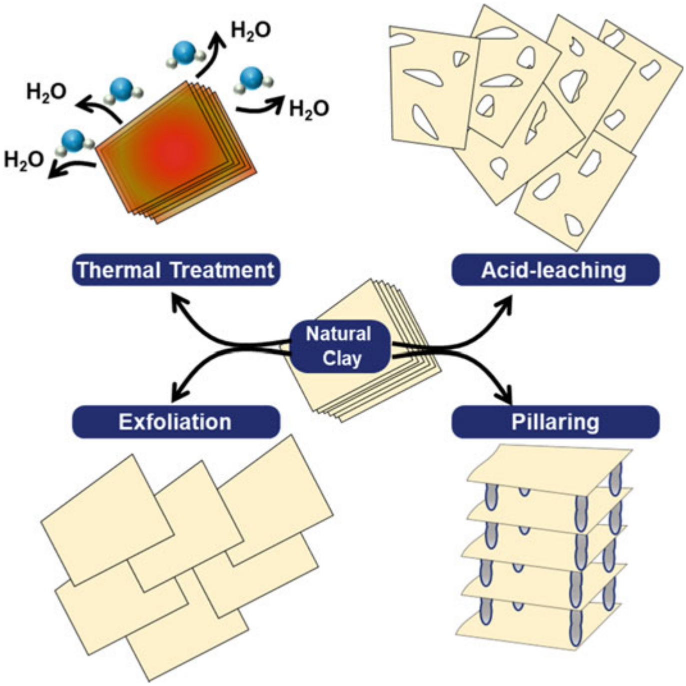


Fig. 3 Strategies employed for natural clay modification

separated, resulting in nanoscale dispersion in the polymer matrix. Acid leaching and pillaring are results of intercalation where an ion or a large molecule like a dye or polymer is physically inserted between two layers of clay. The inter-layer spacing is not significantly impacted during intercalation. Cations in clay minerals can be changed via such ion-exchange reactions to replace the desired ions as active catalytic species. Monovalent and divalent cations in the interlayer region of MMT can be replaced with other ions to produce either homoionic or heteroionic MMT.

3.1 Thermal Treatment

Thermal treatment of kaolinite clays removes water from the structure, causing it to collapse and reconstruct into an amorphous metakaolin [28]. This modifies the catalytic ability of the natural kaolinite, which is negatively affected by the crystalline phase and low specific surface. The typical thermal treatment process occurs in a muffle furnace where kaolin undergoes a calcination process under temperatures ranging from 550 to 800 °C [29]. At temperatures between 100 and 400 °C, a set of –OH groups in the clay mineral separate into O^{2-} and H^+ ions resulting in an abundance of H^+ ions to form water molecules combining with other –OH groups.

These water molecules evaporate from the mineral clay [30]. Again, the mineral clay crystal lattice transforms into a structure analogous to its natural form at 600 °C, rearranging the silica and alumina layers and the O^{2-} ions [31, 32] show that thermal treatment of kaolinite clays at 750 °C produces metakaolin with a higher specific surface area. Moreover, the high-temperature treatment of clays tends to form micro-cracks or widen pores on the surface of clay minerals. The structural modification and the increased porosity warranted through thermal treatment enable the resulting modified clay mineral to act as a catalyst and a supporting material for other catalysts, including organic substances and metals.

3.2 Acid Leaching

Treating clay minerals with acids results in hydrogen ion-exchanged clay minerals. The acid treatment leads to the part or thorough breakdown of layers, broken-edge M–O− bonds, and a reduced particle size of clay platelets. Selective leaching out of the central atoms in tetrahedral and octahedral sheets produces active sites with higher acidity and a larger surface area. The concentration, type of acid, reaction time, and temperature affect the properties of the resulting acidified clay minerals. Acid leaching can introduce guest species into the space between the expandable layers (intercalation). For instance, smectitic clay minerals can absorb guest species ranging in size from a few angstroms to several nanometers into their interlayer space because of their ion exchange capacity and swelling. When Al–O layers are removed from clay, the surface area of the clay increases, allowing active phases to be more evenly distributed. This leads to closer contact between the active sites of the catalyst and reactants and improves the catalytic reaction. One way to modify the Al–Si ratio of clay-based catalysts, such as zeolites, is through a dealumination process using acids [33]. Furthermore, acid leaching can also create meso and macro pores on the clay surface, increasing the pore volume and active metal content. This leads to better control of particle growth and inhibition of catalyst deactivation [33, 34].

3.3 Exfoliation

Exfoliation can be achieved by intercalation, ultrasonication in water [35, 36], and high-energy ball milling [37]. Huang et al. [38] employ isopropanol with poly(oxyethylene-oxypropylene)-amines (POA) as intercalating agents to exfoliate the Na-MMT layers. As clay minerals undergo swelling in water, the positively charged ions in the clay interlayer solubilize, resulting in a net negative charge between the adjacent layers. The electrostatic repulsion between the two identically charged clay layers weakens their bond. The weakened bonds between clay layers get disrupted by the strong vibrations generated from ultrasonication, producing exfoliated clay layers [35, 36]. Also, clay minerals can be exfoliated by high-energy ball milling [37]. Applying energy to clays through the friction and impact in the ball mill disrupts the layered structure, causing them to exfoliate into sheets [36]. The high-energy grinding severs the bonds between the clays, exposing new active surface [39]. Masindi et al. [40] show that high-energy vibratory ball milling doubles South African bentonite clay's BET (Brunauer, Emmett, and Teller) surface area, which improves their water treatment ability. Similarly, Leo et al. [41] report that, under high-energy ball milling, smectite clays experience delamination, leading to increased efficiency in Cd sorption.

3.4 Pillaring

Pillared interlayered clays (PILCs) can be used either as a catalyst support or as a catalyst [42]. Techniques for pillaring clays include using mixed solutions, coordination or organometallic compounds, polymers and surfactants, acid-activated clays, and enhancing PILC acidity [43–45]. The process of pillaring clays involves replacing the cations in the interlayer space of swelling clays with bulkier polyhydroxy metal cations, altering the pillar distance and interlayer spacing. Afterwards, the ion-exchanged clay is calcined, transforming it into metal oxide pillars that are tightly bound to the layers of the clay owing to the penetration of strong inorganic molecules into the interlayer region [46]. Negative charges generated by substituting cations are counterbalanced by alkali or alkaline earth cations inside the galleries, resulting in column-like structures with spaces between them.

PILCs with high porosity can be obtained by using calcination as a post intercalation protocol. The pore size of PILCs can influence the catalytic reaction, as well as resistance to poisoning, temperature, and pressure gradients in the catalyst bed. In addition, active species become immobilised as pillars in PILCs, which prevents them from leaching in a liquid reaction, as opposed to the ion-exchanged clay mineral catalysts. PILCs involving several transition metals such as Fe, Cu, or Mn exhibit exceptional physicochemical properties. Metal oxide PILCs have several interesting properties, such as large surface area, high pore volume, tunable pore size (from micropore to mesopore), high thermal stability, and strong surface acidity [47]. These properties and the ease of incorporating PILCs as active redox components make PILC a better combustion catalyst [48]. PILCs can accommodate larger molecules than zeolites, thus being cheaper replacements [49]. Stacking of the layers leads to a regular van der Waals gap between the layers, known as interlayer. Several recent studies have explored ways to change different aspects of the synthesis process, such as the type of clay used, the intercalating solution, and the drying and calcination steps involved in the manufacture of PILCs.

3.5 Clay Mineral Composites and Nanocomposites

Composites are generally solid multiphase materials designed by combining materials with different properties hence making composites different from other mixture substances like alloys and blends. With the recent advancement in the field of material science and technology, clay composites and polymer–nanoclay composites are getting considerable attention owing to their superior physical, chemical, and structural properties. Granulated clay composites comprising activated carbon-clay composites and cross-linked clay beads [50], Bentonite-alginate composites, and magnetic chitosan/clay beads are some of the emerging clay composites. The major benefits of using clay composites over other adsorbents are as follows:

1. Ability to remove both organic and inorganic contaminants,
2. High sorption capacity,
3. Economic feasibility.

Clay-based composites can be used as adsorbents, catalyst supports, or catalysts for important industrial organic reactions like esterification, alkylation, isomerization, Diels–Alder reactions, coupling reactions, and polymerixation reactions. Clay composites formed with metal oxide semiconductors have shown significant improvements in photocatalytic activity [7]. The introduction of oxide pillars in the interlayer space of MMT and the immobilization of metal oxides or zero-valent metals on the surface of MMT allow MMT to be used in catalytic oxidation, reduction, isomerization, and coupling reactions. Moreover, the formation of Fe, Co, and Si composite pillars enhanced the thermal stability of MMT, making it maintain good crystallinity and ordered interlayer structure at high temperature [51]. The mixing of two or more metal-pillared clay composites has shown selective improvements in the catalytic active sites [52].

The particle size, the shape, and the support material govern the catalytic ability of metal nanoparticles. The agglomeration on supporting clay surfaces, such as bentonite and PILC, can significantly enhance the catalytic activity of the metal nanoparticles. At the nanoscale, the tubular morphology of halloysites facilitates core–shell metal support templates for mesoporous catalysts [53]. Thus, the metal nanoparticles' stability and catalytic efficiency can be significantly improved by forming composites with clay minerals. Clay nanocomposites have good thermal and chemical stability, better mechanical and barrier properties, improved flame retardancy, and have longer lifetime [54, 55].

Polymer/clay nanocomposites are emerging and novel materials with a wide range of applications [6, 56]. The term "Nanocomposites" was coined for the first time for nylon/MMT-based composite by the Toyota Central Research Laboratory. Various polymers can be applied to develop nanocomposites for wastewater treatment, dye removal, petrochemical, and biomedical applications [57]. Bentonite and MMT was utilised as nanofillers in EVA nanocomposite for bioimplants to improve mechanical stability and to lessen cytotoxic activity [58]. According to Murugesan and Scheibel [59] and [60] studies, clay-based polymer nanocomposites have excellent biocompatibility, aid rapid tissue generations, stimulates vascularization, and facilitate sustained drug delivery. Also, they have shape memory and are responsive to stimuli reveal that clay-laden polymer nanocomposite is compatible with blood, non-toxic to cells, support fast tissue regeneration, induces vascularization, is helpful for sustained drug release, has a shape memory effect, and is responsive to stimuli. Further, the nanocomposites can be 3D printed or process with thin film preparation methods to make microfluidic devices and orthopaedic implants, and for drug delivery and tissue engineering applications. Other reports have also suggested that these composites could be used in bone cement, wound healing, and enzyme immobilisation. Clay-impregnated polymeric hydrogels are useful in bioprinting and wearable device development.

4 Environmental Remediation Applications

Clay minerals absorb ionic impurities and act as catalysts in degrading environmental pollutants, making them useful for air, water, and soil pollution management. Their catalytic abilities can be further enhanced through modifications such as calcination, acid activation, and magnetization [61]. The available reactants and the 2D structure of the clay composites render them a higher reactivity [6]. The catalytic activity of natural or modified clay minerals comes from four main sources: Brønsted acidity, Lewis acidity, redox active species, and transition metals or cations [6, 26, 62]. Interlayer cations in clay composites give them Brønsted acidity through proton donation and acceptance. Clay minerals that have undergone cation exchange show potential as catalysts for organic reactions. The preparation and design of modern clay-based catalysts still underpin the utilization of layers and the interlayer of clay minerals. Primarily, the studies concerning developing these catalysts have focused on various guest components and preparation conditions. Generally, the rationale for preparing clay-based composite catalysts can be categorized under four perspectives.

1. The presence of active species.
2. The selective exchange of interlayer ions with active components triggers the catalytic activity.
3. The clay nanostructure endures the functional nanoparticles or clusters.
4. Clay minerals or their derivatives act as catalyst supports.

Given their large surface area and inertness, pillared interlayer clays are ideal for immobilizing metal oxocations, including Fe and Al. In addition, the simplicity of the pillaring technique, excellent stability, and minimal metal ion leaching make pillared interlayer clays suitable heterogeneous Fenton catalysts for use in various environmental remediation procedures. Chang et al. [63] indicate that MMT treated with iron pillars has strong catalytic activity in eliminating methylene blue. Moma et al. [43] effectively utilized Fe–Al-pillared clays as heterogeneous catalysts for phenol peroxide oxidation in water. The use of metal nanoparticles in modified clay composites has also garnered increasing interest in recent research. Combining pillaring methods, some researchers have loaded platinum nanoparticles onto the surface of modified clay minerals [64]. These adjustments to the clay composites provide complex catalysts with better chemical recognition, shape selectivity, stereoselectivity, and region selectivity.

PILCs and intercalated clay catalysts may be modified and employed as a support or promoter through ion exchange. New kinds of supported (heterogeneous) clay catalysts have evolved from advances in intercalation, such as the accommodation of ion-pair salt into the interlayers and the interactions of metal complexes or other organic compounds with MMT. As catalysts for organic synthesis, several metals or metal oxides can be selectively supported on activated clay, PILCs, and PCHs materials [65]. A clay-complex catalyst, such as dinuclear manganese(III) complex $[Mn_2III,III(O)(tpdm)_2(OAc)_2]$ ((tpdm = tris(2-pyridyl)methane)) and manganese(III) acetate $Mn\ (OAc)_3$, performed a catalytic function in the light-driven oxidation of water [66]. Zhou [67] provides a rich discussion on similar clay-based designer catalysts for green and sustainable catalysis. In addition to the structural modifications made to composites, current research has investigated the microwave-assisted Fenton degradation of composites (e.g., [47]).

4.1 Combustion Catalysis

Clay-based composites have become increasingly popular as catalysts for catalytic combustion due to their availability, low cost, high-temperature stability, and environmental friendliness. Among these composites, PILC-based catalysts have been significantly employed for the catalytic combustion of volatile organic compounds (VOCs) such as acetone, benzene, butylamine, chlorobenzene, propene, and trichloroethylene. Such VOCs, if untreated, can significantly contribute to environmental pollution by forming ground-level ozone and fine toxic organic particles [42, 62]. Similarly, exfoliated smectites have been employed to synthesize combustion catalysts that show favourable textural qualities and dispersion of the active catalytic phase [68]. In catalytic experiments of toluene and ethanol combustion using MMT/MnO_2 composites, the clay composites revealed distinct catalytic activity depending on the type of the oxidized organic molecule. In the oxidation of toluene, a correlation was discovered between the catalysts' performance and the materials' reducibility. This association was not detected in the case of ethanol, indicating that another factor affected the effectiveness of the catalytic process. Moreover, lower CEC of the clay mineral resulted in a more significant proportion of K in MnO_2, improving the basicity, which is advantageous for ethanol combustion [42, 62].

Cheng et al. [69] developed La_2O_3 silicon-pillar clay-supported PtO_x nanocrystalline catalysts for benzene combustion using a high-temperature liquid reduction technique. The catalyst showed superior adsorption capacity and thermal stability in benzene combustion when a load of 0.2 wt% Pt and a molar ratio of 0.5:1 La/KSF had the most robust catalytic combustion activity and CO_2 selectivity at lower reaction temperatures (about 200 °C). The catalyst remained stable over a 100-h reaction at 195 °C. The excellent dispersion of Pt particles, the presence of active oxygen species, and the strong reaction characteristics of Pt/LaSPC (0.5%) render the catalyst very effective for benzene combustion [69]. Li et al. [42] discussed the modification of PLCs from a single core to multiple cores and their application to the catalytic combustion of VOCs. In addition, the concept of the modification of PILC, the preparation technique, including the screening type and ratio of the pillar solution, and the improvement of conventional synthesis to a one-step, high-temperature, high-pressure hydrothermal synthesis method (HTHP) have been described. Chen et al. [70] synthesize Al-Ni nanocrystal catalysts utilizing a one-step, high-temperature, high-pressure hydrothermal process. The nanocrystal catalyst supported by AlNi-PILC exhibits anti-sintering and enhanced stability. The exhaustive performance evaluation established the optimal synthesis settings for AlNi-PILC [70]. MnO_2/MMT composites were synthesized effectively using a simple reductive process, including $KMnO_4$ and HCl. Some interlayer Na^+ or Ca^{2+} substitution for K^+ cations occur in clay mineral components. The composites had a mesoporous morphology and a substantial specific surface area in the range of 80–116 $m^2\ g^{-1}$. In the presence of a clay mineral matrix, cryptomelane generated substantially shorter fibres. The reducibility of this form was similarly lower than that of the Mt-free reference sample. Attique et al. [71] prepared Fe-POM/attapulgite catalysts that reduced the pyrolysis temperature from 375 to 310 °C. The Fe-POM/attapulgite clay composites exhibited a higher affinity for lower hydrocarbons (C5-C12), with aliphatic hydrocarbons being most of their composition [71]. In addition, the catalysts improved the production of liquid fuel during the breaking process. For a 50% Fe-POM/attapulgite combination, the greatest yield of liquid oil fraction was 82% with minimal coke. In contrast, non-catalytic pyrolysis produced only 68% liquid oil fractions together with a substantial amount of solid black residue [71].

The strategic combination of selective catalytic oxidation of nitrogen-containing volatile organic compounds (NVOCs) and selective catalytic reduction of the secondary pollutant NO_x might eradicate both NVOCs and NO_x efficiently. To do this, a combination of Cu_xMg_{3-f} $Cu_xMg_{3-x}AlO$ oxides was formulated and evaluated for the selective catalytic oxidation of n-butylamine. The Cu concentration considerably altered the catalytic performance. At 350 °C, $Cu_{0.4}Mg_{2.6}AlO$ exhibited the highest catalytic activity, converting n-butylamine to N_2 with a selectivity of 83% [72]. Ma et al. [73] investigates the usage of two types of spherical SiO_2 materials with varying surface areas as a substrate for Pd nanoparticles introduced via in situ synthesis, wet impregnation, and grafting. The types of support and preparation procedures impacted the catalytic activity of catalysts [73]. The grafting technique yielded more active catalysts due to enhanced Pd dispersion. Nonetheless, these catalysts enhanced NO_x generation. In contrast, in situ synthesized catalysts could burn n-butylamine while exhibiting superior catalytic activity and producing less NO_x [73].

4.2 Water Treatment

Many studies have attempted the removal of phenol using PILCs and bentonite-based materials manufactured at ambient temperature and atmospheric pressure [74]. Al/Fe and Al/Ce/Fe-PILCs were examined as potential catalysts for phenol elimination [74]. Henao-Aguirre et al. [75] produced extrudates from Al/Fe and Al/Ce/Fe pillared bentonite in the form of pellets, Raschig rings, and monoliths using Na- or Ca-bentonite as a binder. The catalyst could be reused for several reaction cycles without a substantial decrease in its catalytic activity, with just a small quantity of Fe leaching from the catalyst into the solution. Al/Fe-PILCs, as synthesized, were proven to be an effective catalyst for industrial wastewater treatment. Using a wet oxidation method, Guo et al. [76] examined Al/Fe-PILC extrudates in packed-bed operations for wastewater treatment. The catalytic oxidation of phenol typically produces aromatic intermediates such as catechol, hydroquinone, and benzoquinones. These intermediates are converted to organic acids such as oxalic acid, formic acid, maleic acid, and fumaric acid. According to reports, the chemical and catalytic capabilities of the powdered produced materials are retained in the extrudate state. The extrudate materials' intrinsic diffusional constraints affect the observed discrepancies in the reaction times necessary for equivalent phenol elimination.

Increasing the adsorption capacity of PILCs significantly boosts the organic contaminant removal rate since adsorption on the surface of the catalyst expedites the removal of organic pollutants by AOPs. Moma et al. [43] produced a unique Al/Cr-pillared MMT clay with outstanding phenol oxidation ability. Complete desorption could be performed at a temperature well below the material's calcination temperature, indicating reusability of the material. Ziyat et al. [77] produced Al-PILCs from Moroccan clay that exhibits high adsorption capability for aqueous thymol removal in wastewater. Tomul et al. (2019) created Ti-pillared bentonite, Cu, Ag, and Fe-modified Ti-pillared bentonite, and Cu/Ti- and Fe/Ti pillared bentonite composites utilizing various Ti sources by direct synthesis or modification after synthesis. Gao et al. [78] demonstrated that NiO/sepiolite may remove methylene blue from aqueous solutions. The adsorption and regeneration efficacy of the adsorbent/catalyst NiO/sepiolite were evaluated using methylene blue. NiO/sepiolite adsorbed with methylene blue was regenerated with oxygen as the methylene blue decayed. The removal of adsorbed water from the outside surface of methylene blue was accomplished with a 15% weight loss at 100 °C. At 350 °C, catalysts adsorbed with the dye no longer exhibited weightlessness after 18 min. The mass loss of 4% was in good agreement with the methylene blue adsorption quantity on NiO/sepiolite at saturation (39.06 mg/g) [78]. Adsorption kinetics and equilibrium adsorption isotherm fitted pseudo-second-order kinetic model and Langmuir isotherm model, respectively. Table 1 contains selected examples of literature containing clay catalysts in removing dye from wastewater.

Table 1 Clay composite-based catalysts used in the removal of dye in wastewater

Composite	Summary	Reference(s)
Fe_3O_4/bentonite	Fe_3O_4 nanoparticles were used to magnetize bentonite. The resulting composite shows high adsorption capacity and an efficient adsorption of the organic contaminants where the equilibrium could be established within 20 min. Gamma-irradiation of the absorbent enables its re-use. The potential application includes treatment of coloured wastewaters	[79, 80]
Iron oxide/activated MMT	A 0.5 g of Fe_3O_4/activated MMT (Fe_3O_4/MMT) nanocomposite removed 99.47% of the MB from a 120 mg L^{-1} solution at 293 K and at an original solution pH of 7.37 in 25 min. The absorbent could be used for five cycles with 80% or more efficiency	[63]
Sodium eicosenoate (SEIA, anionic surfactant) and cetyltrimethylammonium chloride modified magnetic MMT (Fe_3O_4-CTMAC/SEIA-Mt)	Among the examined composite systems, Fe_3O_4-CTMAC/SEIA-Mt showed a superior adsorption capacity. The adsorbent of Fe_3O_4-CTMAC/SEIA-Mt can be easily separated from the reaction mixture by an external magnetic field. The adsorption of MB on Fe_3O_4-CTMAC/SEIA-Mt was endothermic and it was carried out as a spontaneous process	[81]
Spherical montmorillonite-supported nano-silver	The loading of silver nanoparticles with 40 nm in diameter was 15.2 wt% and the specific surface area of this prepared spherical MMT-supported silver nanoparticles catalyst was 45.3 m^2/g. The prepared catalyst with quickly self-sedimentary property in aqueous solution was conveniently recovered and reused without any devices involves. The catalytic performance of prepared catalyst were almost unaltered after five cycles	[82]
7% Fe_3O_4/kaolinite	A novel and simple solid-state synthetic method of producing Fe_3O_4/kaolinite nanocomposites was developed for enhanced adsorptive removal of cationic and anionic dyes. The obtained Fe_3O_4/kaolinite nanocomposite containing 7 mass% Fe_3O_4 exhibited the best performance. The dye-removal ability of kaolinite could be improved significantly by modification with moderate amount of Fe_3O_4	[83]

(continued)

Table 1 (continued)

Composite	Summary	Reference(s)
Alginate/natural bentonite	Hybrid beads were prepared from natural bentonite and alginate. Alginate-to-clay ratios was varied (1/1; 1/2 and 1/3). The results show monolayer and homogeneous adsorption. Regeneration study showed that dyes were successfully desorbed from A-B 1/1 and A-B 1/3 with removal percentages of 99.65% and 86.2%, respectively, in the first cycle	[84]
Polyvinyl alcohol/ carboxymethyl cellulose hydrogels reinforced with graphene oxide and bentonite	Eco-friendly polyvinyl alcohol/carboxymethyl cellulose (isolated from pineapple peel) hydrogels reinforced with graphene oxide and bentonite were prepared. After introducing graphene oxide and bentonite into the hydrogels, the maximum adsorption capacity calculated from the Langmuir isotherm model reached 172.14 mg/g at 30 °C. The absorbents displayed good reusability for the efficient removal of anionic dyes in wastewater treatment	[85]
Hydrogel based on katira gum-clpoly(acrylic acid-co-N, Ndimethylacrylamide) incorporated bentonite (BT) nanoclay	Various nanocomposite hydrogels (KGNCH-1 to KGNCH-4) are prepared by varying weight percentage of bentonite clay. The best one is selected (KGNCH-3) with respect to their highest swelling percentage in aqueous medium. The adsorption of cationic dyes onto the KGNCH-3 is found to be pH dependent. The absorbent also exhibits excellent regeneration capacity at different pH using five cycles of adsorption–desorption studies	[86]
MMT/graphene oxide	Composite structure of MMT with graphene oxide (GO) or reduced graphene oxide (rGO) was successfully synthesised by grafting with 3-aminopropyl triethoxysilane (APTES) and hydrazine hydrate reduction. Mechanism analysis suggested that the high absorption performance of the composite was determined by the high specific surface area, oxygenic groups of GO, high adsorption capacity of MMT, and the synergistic effect between the Mt and graphene oxide nanosheets	[87]

4.3 Biodiesel Production

Biodiesel is a sustainable alternative to crude oil that can be synthesized from both edible and non-edible vegetable oil, animal fats, and fungal and algal sources. Biodiesel contains long-chain fatty acid alkyl esters, which result from the transesterification reaction between alcohol and triacylglycerol’s in the presence of a catalyst.

Many important parameters including biodiesel yield, reaction conditions, and post-separations steps that influence the economic viability of biodiesel process are influenced by the catalyst. Clay-based catalysts in biodiesel production prevent inconveniences occurring with homogeneous and other solid catalysts including soap formation, non-reusability, leaching, swelling, and extensive pretreatment of biomass [4].

Also, clay-based catalysts produce low-cost and high-quality biodiesel yield [88].

Munir et al. [89] reported of gaining the highest yield of 85% biodiesel with cadmium and manganese-impregnated MMT clay catalyst (with 4% catalytic loading) from Prunus Cerasoides seed oil from transesterification reaction. Similarly, 98.5% of biodiesel yield was achieved with sulphonated phenyl silane MMT catalyst from Jatropha seed oil and 89.8% from castor seed oil transesterification. Reusability of clay-based catalysts in biodiesel production improves the catalyst both economic and environmental performance of the process. For an example, K_2CO_3-loaded Palygorskite catalysts could be used upto 8th cycles to transesterification palm oil managed to generate a yield above 80% [90].

MMT-derived catalysts are the most common as catalysts in biodiesel production, while bentonite, kaolinite, and playgorskite-derived catalysts are also generally used. Many catalysts preparation methods including wet impregnation, hydrothermal synthesis, mechanical/thermal/acid activation, ion-exchange, and pillaring are employed to derive clay catalysts for biodiesel production [4]. Table 2 shows the details of selected clay catalysts, catalyst preparation methods, optimum reaction conditions, reusability, biodiesel source, and yield. Here, bentonite/zeolite-P composite (B/ZP) was synthesized by simple alkaline hydrothermal treatment at 150 °C for 4 h and characterized by different analytical techniques. The composite was introduced as a low-cost catalyst of enhanced physiochemical properties and catalytic activity in the transesterification of palm oil into biodiesel. The catalyst is of higher activities than several homogenous and heterogeneous catalysts and can be reused several times with high catalytic activity especially using an organic solvent either by normal stirring or under the ultrasonic irradiation. The physicochemical specification of the obtained biodiesel by both methods matches the requirements of STM D-6571 and EN 14214 international standards.

Shan et al. [90] produce biodiesel from plum waste seed oil using a catalyst supported on low-cost Bentonite clay. For this purpose, bentonite-potassium ferricyanide, White pocha-potassium ferricyanide, Granite-potassium ferricyanide, Sindh clay-potassium ferricyanide, and Kolten-potassium ferricyanide composites were prepared. The highest biodiesel yield was observed when calcinated Bentonite-potassium ferricyanide composite was used as the catalyst support. The increase in the average crystal size of the composite, granted by the calcination (as supported by XRD results), and the changes in the surface characteristics (as revealed by SEM images) have provided a comparatively greater surface area for reactants for successful conversion into biodiesel.

Table 2 Details of selected biodiesel processes that employed clay catalysts

Clay mineral	Catalyst	Catalysts preparation method	Cal T °C	Cal time (h)	Oil source	Optimized reaction conditions for biodiesel production				Yield	Catalysts reusability (No of cycles)	Reference
						Cat conc (wt%)	Oil:methanol	T (°C)	Time			
MMT	Cu modified MMT	Wet impregnation	500	Not mentioned	Raphnus raphanistrum L	3.5%	1:15	150	5 h	83%	5	[91]
MMT	Zirconium-modified MMT	Wet impregnation	500	Not mentioned	*Lepidium perfoliatum* Linn seed oil	3.5	1:15	135	4 h	88%	3	[88]
MMT	Cd and Mn impregnated MMT	Wet impregnation	500	NM	Prunus Cerasoides D Don	4%	1:12	120	5 h	85%	–	[89]
Bentonite	Sodium methoxide supported bentonite	Impregnation	350	3	Waste sunflower oil	2%	1:12	55	70 min	94.3%	More than 4 (upto 80% yield)	[92]
Bentonite	NaOH/bentonite	Wet impregnation	60	12	Waste cooking oil	0.5%	1:15	55	2 h	72%	–	[93]
Kaolinite	Zeolite LTA-kaolin	Hydrothermal	400	6	Triolein	72%	1:36.6 (mass ratio)	62.9	146 min	92.8 ± 4.0%	3	[94]
Kaolinite	K_2O_3/kaolin (20 wt% K_2CO_3)	Wet impregnation	550	3	Sunflower oil	5 wt%	1:6	65	4 h	95.3 ± 1.2%		[95]
Palygorskite	Ni/palygorskite	Deposite precipitation	500	2.5	Waste cooking oil	30 Ni/P%	10 ml:0.33 g	65	4 h	83%		[96]

(continued)

Table 2 (continued)

Clay mineral	Catalyst	Catalysts preparation method	Cal T °C	Cal time (h)	Oil source	Optimized reaction conditions for biodiesel production				Yield	Catalysts reusability (No of cycles)	Reference
						Cat conc (wt%)	Oil:methanol	T (°C)	Time			
Palygorskite	K_2CO_3/palygorskite 40% K_2CO_3 loading on palygorskite	Wet impregnation	550	4	Palm oil	5%	1:12	65	3.5 h	97.0%	More than 8 (resulting yield above 80%)	[90]
Sepiolite	NaOH impregnated sepiolite	Wet impregnation	500	5	Canola oil	6 wt%	1:9	60	3 h	80.93%	ND	[97]
Sepiolite	$K_2CO_3/\gamma\text{-}Al_2O_3$/sepiolite magnetic ($Fe_3O_4$) catalyst	Mechanical activation	500	4	Sunflower oil	5 wt%	1:12	80	4 h	88%	ND	[98]

4.4 Photocatalysis

Photochemistry is another field where highly performing nanocatalysts are required. Technological innovations resulting in efficient, cheap, and stable photocatalysts are the key for development of solar energetics. Typically, the high percentages of SiO_2 and Al_2O_3 in the Clay mineral compositions render them with high energy band gaps (e.g., 9 and 8.8 eV) that hinder their use as efficient materials to capture solar energy. Yet, MMTs have shown the potential to absorb up to 300 nm of UV light and visible light irradiations [99]. The light harvesting potential of clay can be significantly improved by creating composites with photoreactive materials, such as metal oxides (WO_3, TiO_2, Fe_2O_3), non-metal oxide semiconductors or Non-metal oxide semiconductors consist of materials such as g-C_3N_4. In such applications, clays induce spatial charge separation and, consequently, an extended lifespan of electron/hole pairs, resulting in enhanced photocatalytic activity via the promotion of heterojunction formation over composite photocatalysts.

Kaolinite and MMT have been extensively employed to support different semiconductor photocatalysts, therefore producing composites and obtaining effective conversion of reactants under solar irradiation. The modified clays can enhance the photochemical process by facilitating the creation of composites [100]. In addition to a wide surface area and an active surface hydroxyl group, the layered structure of clay-based photocatalysts allows extra room to expand their use. Recently, clay minerals have been utilized more often in the production of hybrid photocatalysts. Typically, the photocatalytic uses of metal oxides are hindered by the rapid charge recombination of charge carriers, poor surface area, inactivity under visible light, inefficiency, and expensive post-treatment recovery. Clay nanocomposites have substantially increased the light-gathering capability of metal oxides. Due to the increased availability of active surface sites and decreased particle aggregation, metal oxide nanoparticles supported on clay minerals exhibit enhanced photocatalytic activity. For instance, dispersing TiO_2 nanoparticles on the surfaces of clay minerals increases the photocatalytic activity of TiO_2 by increasing the number of active surface sites and decreasing the concentration of TiO_2 nanoparticles [101]. The addition of metals such as copper, silver, gold, nickel, and platinum to MMT/TiO_2 nanocomposites can enhance its photocatalytic yields and selectivity [102, 103].

Clay composites have been used for photocatalysis in a variety of applications, including the degradation of organic contaminants when exposed to visible light [104]. Under visible light irradiation, the sepiolite/CN/Pd(0) composite can operate as a possible catalyst for degrading organic pollutants in wastewater. Chuaicham et al. [100] develop a composite of natural sepioliteclay and synthetic graphitic carbon nitride (CN) mixed with dispersed palladium nanoparticles for the efficient photocatalytic degradation of ciprofloxacin (CIP) under visible light irradiation. The sepiolite/CN composite (SC30%) displayed superior activity than pristine sepiolite and CN, resulted from the generation of new electron trap states in the interfacial contract between sepiolite and CN to suppress the charge recombination of CN. Furthermore, the well-dispersed of 1 wt% Pd nanoparticles in the SC30% composite collectively enhanced CIP degradation by avoiding the recombination of photogenerated electrons and holes. Titania is one of the most popular photocatalyst for decomposing organic compounds due to its strong photocatalytic activity, chemical and biological inertness, and high photochemical stability. The production of nano-architecturally designed photocatalysts on the base of natural aluminosilicate clays and metal sulphides is a very promising direction for industrial applications.

Photocatalysis is a potential approach for producing H_2 since it just requires water and a catalyst in the presence of ultraviolet or visible light. Using a low-cost, highly active, and photostable g-C_3N_4/MMT/TiO_2 composite can improve the efficiency of photocatalytic water splitting. Increased dispersion and separation of charges by MMT and an adequate band structure of the 2D/2D/0D g-C_3N_4/MMT/TiO_2 composite catalyst functional under light irradiation can generate much higher volumes of H_2. MMT acted as a metal, retaining electrons and preventing their recombination for enhanced H_2 evolution. Due to the significant dispersion of g-C_3N_4/MMT/TiO_2 across the MMT structure, the stability test demonstrated outstanding long-term activity over g-C_3N_4/MMT/TiO_2 composites [105]. MMT-distributed Au/TiO_2 nanocomposite has shown rapid photocatalytic reduction of CO_2 to CO, CH_4, and H_2 [102, 103]. According to Tahir [102, 103], the favourable interaction between MMT transition metals and Au ions and the fast adsorption–desorption process has positively supported this conversion process [102, 103]. Similarly, ZnS/MMT nanocomposite demonstrated photocatalytic CO_2 reduction by H_2O to CO, CH_4, and H_2. Multiwall carbon nanotubes (MWCNTs) with modified TiO_2 1D/0D heterojunction distributed in 2D MMT nanoclay composites yielded H_2 evolution rate of 1888 ppm h^{-1}. The H_2 evolution via electrophilic substitution reaction has been improved by the MMT-dispersed TiO_2 catalysts that support Ni and Ni-CaO. Enhanced metal dispersion with minimized sintering and coke formation effects have enhanced the high activity and stability of these catalysts. For instance, Tahir [102, 103] have reported NiO loaded over MMT support yielding higher H_2 production from ethanol steam reforming. Vermiculite clay-based catalysts were also used for photocatalytic CO_2 reduction to produce solar fuels. Valaskova and co-workers first ball-milled the raw vermiculite, followed by loading of α-Fe_2O_3 and subsequent calcination. It was noted that the α-Fe_2O_3/Ver composite calcined at 500 °C showed meliorated photoactivity for CO formation due to the oxygen vacancy-rich surface that acts as electron traps. This in turn prevents the recombination of electron/hole pairs, which prolongs the lifetime of the charge carrier for the reduction of CO_2 to CO. Also, the introduction of vermiculite boosted the specific surface area, which was believed to enhance the light harvesting capability of the composite [106] (Table 3).

Table 3 Clay composite based photocatalysts in H_2 evolution

Photocatalyst	Reference	Composite	Irradiation condition
HNTs-based	[107]	$Cd_{0.5}Zn_{0.5}S$	Xenon lamp (λ > 400 nm)
	[108]	CdS	LED lamp (λ = 450 nm)
MMT-based	[109]	TiO_2	Visible light
	[110]		
	[111]	pCN-TiO_2	
Palygorskite/attapulgite-based composites	[112]	MoS_x nanodots	

5 Concluding Remarks

Clay-based composite catalysts show great potential in remediating environmental issues. These catalysts, which are primarily heterogeneous in nature, abate heavy metals from water by strongly interacting with pollutants and desorbing them by altering pH or temperature. Also, these materials' photocatalytic activity has expedited the production processes of H_2 evolution and carbon degradation and resulted in a paradigm shift in sustainable energy-related research. Given the increasing demand for clay minerals, unsustainable rapid mining of these minerals has caused severe environmental pollution that negatively affects species living on land and aquatic systems. The suspended clay and silt generated from unsustainable mining activities affect the development and reproduction of marine species. Moreover, natural clay may contain toxic inorganic metal ions that should be freed before preparing clay minerals for water treatment. Modifying clay using concentrated inorganic acids produces acidic effluent, equipment damage, and operational hazards, which harm the environment. Since the potential alternatives to inorganic acids, such as carboxylic and sulfonic acids, can minimize these issues, further studies should focus on the effects of these alternative acids on the layer, interlayer, and catalytic mechanism of modified clay composites. The limited mechanical strength, temperature and pressure resistance, and recycling issues are critical challenges associated with clay composite catalysts. Future studies should address these challenges while improving catalyst efficiency and reusability. Also, most of the synthesis procedures of the clay composites reported in the literature take time and expensive equipment like centrifuges and autoclaves. Such demanding processes limit the industrial-scale applicability of these catalysts. The limited reproducibility challenges the relevance of these novel methods in local clay reserves in underdeveloped regions.

References

1. Anastas, P.T., Kirchhoff, M.M., Williamson, T.C.: Catalysis as a foundational pillar of green chemistry. Appl. Catal. A **221**(1–2), 3–13 (2001)
2. Baloyi, J., Ntho, T., Moma, J.: Synthesis and application of pillared clay heterogeneous catalysts for wastewater treatment: a review. RSC Adv. **8**(10), 5197–5211 (2018)
3. Mavrikos, A., Papoulis, D., Todorova, N., Papailias, I., Trapalis, C., Panagiotaras, D., Chalkias, D.A., Stathatos, E., Gianni, E., Somalakidi, K., Sygkridou, D.: Synthesis of Zn/Cu metal ion modified natural palygorskite clay–TiO_2 nanocomposites for the photocatalytic outdoor and indoor air purification. J. Photochem. Photobiol., A **423**, 113568 (2022)
4. Nawaz, S., Ahmad, M., Asif, S., Klemeš, J.J., Mubashir, M., Munir, M., Zafar, M., Bokhari, A., Mukhtar, A., Saqib, S., Khoo, K.S.: Phyllosilicate derived catalysts for efficient conversion of lignocellulosic derived biomass to biodiesel: a review. Biores. Technol. **343**, 126068 (2022)
5. Selvitepe, N., Balbay, A., Saka, C.: Optimisation of sepiolite clay with phosphoric acid treatment as support material for CoB catalyst and application to produce hydrogen from the $NaBH_4$ hydrolysis. Int. J. Hydrogen Energy **44**(31), 16387–16399 (2019)
6. Zou, Y., Hu, Y., Shen, Z., Yao, L., Tang, D., Zhang, S., ... Wang, X.: Application of aluminosilicate clay mineral-based composites in photocatalysis. J. Environ. Sci. **115**, 190–214 (2022)
7. Fan, W.K., Tahir, M.: Structured clay minerals-based nanomaterials for sustainable photo/thermal carbon dioxide conversion to cleaner fuels: a critical review. Sci. Total Environ. 157206 (2022)
8. Barakan, S., Aghazadeh, V.: The advantages of clay mineral modification methods for enhancing adsorption efficiency in wastewater treatment: a review. Environ. Sci. Pollut. Res. **28**(3), 2572–2599 (2021)
9. Lange, J.P.: Performance metrics for sustainable catalysis in industry. Nat. Catal. **4**(3), 186–192 (2021)
10. Zhang, W., Zhang, R., Wu, C., Goh, A.T., Wang, L.: Assessment of basal heave stability for braced excavations in anisotropic clay using extreme gradient boosting and random forest regression. Undergr. Space **7**(2), 233–241 (2022). https://doi.org/10.1016/j.undsp.2020.03.001
11. Liu, X., Wang, W., Du, C., Su, Y.: Synergistic activation of peroxymonosulfate via oxygen vacancy-rich $Co_xMn_{3-x}O_4$/MMT catalyst for environmental remediation. Appl. Clay Sci. **228**, 106625 (2022)
12. Feng, Y., Chu, G., Xiao, B., Li, R., Deng, C., Li, G., Shi, H.: Chlorite mineralogy, geochemistry and exploration implications: a case study of the Xiaokelehe porphyry Cu-Mo deposit in NE China. Ore Geol. Rev. **140**, 104568 (2022)
13. Anggraini, V., Dassanayake, S., Emmanuel, E., Yong, L.L., Kamaruddin, F.A., Syamsir, A.: Response surface methodology: the improvement of tropical residual soil mechanical properties utilizing calcined seashell powder and rreated coir fibre. Sustainability **15**(4), 3588 (2023). https://doi.org/10.3390/su15043588
14. Alaba, P.A., Sani, Y.M., Daud, W.M.A.W.: Kaolinite properties and advances for solid acid and basic catalyst synthesis. RSC Adv. **5**(122), 101127–101147 (2015)
15. Cao, Z., Wang, Q., Cheng, H.: Recent advances in kaolinite-based material for photocatalysts. Chin. Chem. Lett. **32**(9), 2617–2628 (2021)
16. Ayodele, O.B., Abdullah, A.Z.: Exploring kaolinite as dry methane reforming catalyst support: influences of chemical activation, organic ligand functionalization and calcination temperature. Appl. Catal. A **576**, 20–31 (2019)
17. Rosadi, I., Athikaphan, P., Chantanachat, P., Neramittagapong, A., Neramittagapong, S.: The catalytic activity of Co/kaolinite catalyst for dimethyl ether synthesis via methanol dehydration. Energy Rep. **6**, 469–473 (2020)
18. Prasetyoko, D., Santoso, M., Qoniah, I., Leaw, W.L., Firda, P.B., Nur, H.: A review on synthesis of kaolin-based zeolite and the effect of impurities. J. Chin. Chem. Soc. **67**(6), 911–936 (2020)

19. Jinhua, W., Xiang, Z., Bing, Z., Yafei, Z., Rui, Z., Jindun, L., Rongfeng, C.: Rapid adsorption of Cr (VI) on modified halloysite nanotubes. Desalination **259**(1–3), 22–28 (2010)
20. Anastopoulos, I., Mittal, A., Usman, M., Mittal, J., Yu, G., Núñez-Delgado, A., Kornaros, M.: A review on halloysite-based adsorbents to remove pollutants in water and wastewater. J. Mol. Liq. **269**, 855–868 (2018)
21. Pandey, P., Saini, V.K.: Pillared interlayered clays: sustainable materials for pollution abatement. Environ. Chem. Lett. **17**(2), 721–727 (2019)
22. Sun, B., Khan, F.A., Süss-Fink, G., Therrien, B.: Metal catalysts intercalated in smectite clays. In: Encapsulated Catalysts, pp. 387–441. Academic Press (2017)
23. Zhang, T., Wang, W., Zhao, Y., Bai, H., Wen, T., Kang, S., ... Komarneni, S.: Removal of heavy metals and dyes by clay-based adsorbents: from natural clays to 1D and 2D nano-composites. Chem. Eng. J. **420**, 127574 (2021)
24. Borah, D., Nath, H., Saikia, H.: Modification of bentonite clay & its applications: a review. Rev. Inorg. Chem. **42**(3), 265–282 (2022)
25. Amaya, J., Bobadilla, L., Azancot, L., Centeno, M., Moreno, S., Molina, R.: Potentialization of bentonite properties as support in acid catalysts. Mater. Res. Bull. **123**, 110728 (2020)
26. Zhou, C.H., Zhou, Q., Wu, Q.Q., Petit, S., Jiang, X.C., Xia, S.T., ... Yu, W.H.: Modification, hybridization and applications of saponite: an overview. Appl. Clay Sci. **168**, 136–154 (2019)
27. Abukhadra, M.R., Sayed, M.A.: K^+ trapped kaolinite (Kaol/K^+) as low cost and eco-friendly basic heterogeneous catalyst in the transesterification of commercial waste cooking oil into biodiesel. Energy Convers. Manage. **177**, 468–476 (2018)
28. Ilić, B.R., Mitrović, A.A., Miličić, L.R.: Thermal treatment of kaolin clay to obtain metakaolin. Hem. Ind. **64**(4), 351–356 (2010)
29. Souri, A., Golestani-Fard, F., Naghizadeh, R., Veiseh, S.: An investigation on pozzolanic activity of Iranian kaolins obtained by thermal treatment. Appl. Clay Sci. **103**, 34–39 (2015). https://doi.org/10.1016/j.clay.2014.11.001
30. Cheng, Z., Feng, B., Chen, Z., Zheng, J., Li, J., Zuo, S.: La_2O_3 modified silica-pillared clays supported PtOx nanocrystalline catalysts for catalytic combustion of benzene. Chem. Eng. J. **392**, 123747 (2020). https://doi.org/10.1016/j.cej.2019.123747
31. Kusrini, E., Wicaksono, W., Gunawan, C., Daud, N.Z.A., Usman, A.: Kinetics, mechanism, and thermodynamics of lanthanum adsorption on pectin extracted from durian rind. J. Environ. Chem. Eng. **6**(5), 6580–6588 (2018). https://doi.org/10.1016/j.jece.2018.10.018
32. Sun, Q., Zhang, W., Qian, H.: Effects of high temperature thermal treatment on the physical properties of clay. Environ. Earth Sci. **75**, 1–8 (2016). https://doi.org/10.1007/s12665-016-5402-2
33. Alshahidy, B.A., Abbas, A.S.: Comparative study on the catalytic performance of a 13X zeolite and its dealuminated derivative for biodiesel production. Bull. Chem. React. Eng. Catal. **16**(4), 763–772 (2021)
34. Rubtsova, M., Smirnova, E., Boev, S., Kotelev, M., Cherednichenko, K., Vinokurov, V., Lvov, Y., Glotov, A.: Nanoarchitectural approach for synthesis of highly crystalline zeolites with a low Si/Al ratio from natural clay nanotubes. Microporous Mesoporous Mater. **330**, 111622 (2022). https://doi.org/10.1016/j.micromeso.2021.111622
35. Chen, T., Yuan, Y., Zhao, Y., Rao, F., Song, S.: Preparation of montmorillonite nanosheets through freezing/thawing and ultrasonic exfoliation. Langmuir **35**(6), 2368–2374 (2019)
36. Zhu, T.T., Zhou, C.H., Kabwe, F.B., Wu, Q.Q., Li, C.S., Zhang, J.R.: Exfoliation of montmorillonite and related properties of clay/polymer nanocomposites. Appl. Clay Sci. **169**, 48–66 (2019)
37. Galimberti, M., Coombs, M., Cipolletti, V., Spatola, A., Guerra, G., Lostritto, A., Giannini, L., Pandini, S., Riccò, T.: Delaminated and intercalated organically modified montmorillonite in poly (1, 4-cis-isoprene) matrix. Indications of counterintuitive dynamic-mechanical behavior. Appl. Clay Sci. **97**, 8–16 (2014)
38. Huang, T.K., Chiou, J.Y., Wang, Y.C., Hsieh, K.H., Lin, J.J.: Unusual exfoliation of layered silicate clays by non-aqueous amine diffusion mechanism. J. Polym. Res. **23**(8) (2016). https://doi.org/10.1007/s10965-016-1035-0

39. Cagnetta, G., Robertson, J., Huang, J., Zhang, K., Yu, G.: Mechanochemical destruction of halogenated organic pollutants: A critical review. J Hazard. Mater. **313**, 85–102 (2016). https://doi.org/10.1016/j.jhazmat.2016.03.076
40. Masindi, V., Gitari, M.W., Tutu, H., DeBeer, M.: Efficiency of ball milled South African bentonite clay for remediation of acid mine drainage. J. Water Process. Eng. **8**, 227–240 (2015)
41. Di Leo, P., Pizzigallo, M.D.R., Ditaranto, N., Terzano, R.: Cadmium decontamination through ball milling using an expandable clay mineral. Appl. Clay Sci. **182**, 105256 (2019)
42. Li, J., Hu, M., Zuo, S., Wang, X.: Catalytic combustion of volatile organic compounds on pillared interlayered clay (PILC)-based catalysts. Curr. Opin. Chem. Eng. **20**, 93–98 (2018)
43. Moma, J., Baloyi, J., Ntho, T.: Synthesis and characterization of an efficient and stable Al/Fe pillared clay catalyst for the catalytic wet air oxidation of phenol. RSC Adv. **8**(53), 30115–30124 (2018)
44. Zuo, S., Yang, P., Wang, X.: Efficient and environmentally friendly synthesis of AlFe-PILC-supported MnCe catalysts for benzene combustion. ACS Omega **2**(8), 5179–5186 (2017)
45. Li, J., Zuo, S., Yang, P., Qi, C.: Study of CeO_2 modified AlNi mixed pillared clays supported palladium catalysts for benzene adsorption/desorption-catalytic combustion. Materials **10**(8), 949 (2017)
46. Cardona, Y., Vicente, M.A., Korili, S.A., Gil, A.: Progress and perspectives for the use of pillared clays as adsorbents for organic compounds in aqueous solution. Rev. Chem. Eng. (2020)
47. Ewis, D., Ba-Abbad, M.M., Benamor, A., El-Naas, M.H.: Adsorption of organic water pollutants by clays and clay minerals composites: a comprehensive review. Appl. Clay Sci. **229**, 106686 (2022)
48. Vicente, M.A., Gil, A., Bergaya, F.: Pillared clays and clay minerals. In: Handbook of Clay Science, pp. 523–557. Elsevier (2013)
49. Lal, R., Follett, R.F., Stewart, B.A., Kimble, J.M.: Soil carbon sequestration to mitigate climate change and advance food security. Soil Sci. **172**(12), 943–956 (2007). https://doi.org/10.1097/ss.0b013e31815cc498
50. Lahcini, M., Elhakioui, S., Szopinski, D., Neuer, B., El Kadib, A., Scheliga, F., Raihane, M., Calleja, F.B., Luinstra, G.A.: (2016) Harnessing synergies in tin-clay catalyst for the preparation of poly (ε-caprolactone)/halloysite nanocomposites. Eur. Polym. J. **81**, 1–11.(2016). https://doi.org/10.1016/j.eurpolymj.2016.05.014
51. Fang, L., Wang, L., Zhou, T., Liu, L., Zhou, J., Li, M.: Preparation and characterization of Fe, Co, Si-pillared montmorillonites with aminosilanes as silicon pillars precursor. Appl. Clay Sci. **141**, 88–94 (2017)
52. Chmielarz, L., Kowalczyk, A., Skoczek, M., Rutkowska, M., Gil, B., Natkański, P., ... Ryczkowski, J.: Porous clay heterostructures intercalated with multicomponent pillars as catalysts for dehydration of alcohols. Appl. Clay Sci. **160**, 116–125 (2018)
53. Lazzara, G., Cavallaro, G., Panchal, A., Fakhrullin, R., Stavitskaya, A., Vinokurov, V., Lvov, Y.: An assembly of organic-inorganic composites using halloysite clay nanotubes. Curr. Opin. Colloid Interface Sci. **35**, 42–50 (2018)
54. El-Fattah, M.A., El Saeed, A.M., Dardir, M.M., El-Sockary, M.A.: Studying the effect of organo-modified nanoclay loading on the thermal stability, flame retardant, anti-corrosive and mechanical properties of polyurethane nanocomposite for surface coating. Progr. Org. Coat. **89**, 212–219 (2015). https://doi.org/10.1016/j.porgcoat.2015.09.010
55. Lecouvet, B., Gutierrez, J.G., Sclavons, M., Bailly, C.: Structure–property relationships in polyamide 12/halloysite nanotube nanocomposites. Polym. Degrad. Stab. **96**(2), 226–235 (2011). https://doi.org/10.1016/j.polymdegradstab.2010.11.006
56. Amiri, S.: Preparation and characterization of nanoclay-based (Na-MMT and bentonite) polyacrylamide hydrogels as water shut-off agent for enhanced oil recovery. SILICON **11**(3), 1193–1203 (2019)

57. Bharadwaj, R.K., Mehrabi, A.R., Hamilton, C., Trujillo, C., Murga, M., Fan, R., Chavira, A., Thompson, A.K.: Structure–property relationships in cross-linked polyester–clay nanocomposites. Polymer **43**(13), 3699–3705 (2002). https://doi.org/10.1016/S0032-3861(02)00187-8
58. Mohammed Fitri, T.F., Osman, A.F., Alosime, E.M., Othman, R., Hashim, F., Abdullah, M.A.A.: Biomedical PEVA nanocomposite with dual clay nanofiller: cytotoxicity, mechanical properties, and biostability. Polymers **13**(24), 4345. https://doi.org/10.3390/polym13244345
59. Murugesan, S., Scheibel, T.: Copolymer/clay nanocomposites for biomedical applications. Adv. Funct. Mater. **30**(17), 1908101 (2020). https://doi.org/10.1002/adfm.v30.17. https://doi.org/10.1002/adfm.201908101
60. Murugesan, S., Scheibel, T.: Chitosan-based nanocomposites for medical applications. J. Polym. Sci. **59**(15), 1610–1642 (2021). https://doi.org/10.1002/pola.v59.15. https://doi.org/10.1002/pol.20210251
61. Benna, M., Kbir-Ariguib, N., Clinard, C., Bergaya, F.: Static filtration of purified sodium bentonite clay suspensions. Effect of clay content. Appl. Clay Sci. **19**(1–6), 103–120 (2001). https://doi.org/10.1016/S0169-1317(01)00050-3
62. Serwicka, E.M.: Titania-clay mineral composites for environmental catalysis and photocatalysis. Catalysts **11**(9), 1087 (2021)
63. Chang, J., Ma, J., Ma, Q., Zhang, D., Qiao, N., Hu, M., Ma, H.: Adsorption of methylene blue onto Fe_3O_4/activated montmorillonite nanocomposite. Appl. Clay Sci. **119**, 132–140 (2016)
64. Zhang, Q., Zhang, T., He, T., Chen, L.: Removal of crystal violet by clay/PNIPAm nanocomposite hydrogels with various clay contents. Appl. Clay Sci. **90**, 1–5 (2014). https://doi.org/10.1016/j.clay.2014.01.003
65. Ding, X., Henrichs, S.M.: Adsorption and desorption of proteins and polyamino acids by clay minerals and marine sediments. Mar. Chem. **77**(4), 225–237. https://doi.org/10.1016/S0304-4203(01)00085-8
66. Berends, H.M., Homburg, T., Kunz, I., Kurz, P.: K10 montmorillonite supported manganese catalysts for the oxidation of water to dioxygen. Appl. Clay Sci. **53**(2), 174–180 (2011)
67. Zhou, C.H.: An overview on strategies towards clay-based designer catalysts for green and sustainable catalysis. Appl. Clay Sci. **53**(2), 87–96 (2011)
68. Napruszewska, B.D., Michalik-Zym, A., Rogowska, M., Bielańska, E., Rojek, W., Gaweł, A., Wójcik-Bania, M., Bahranowski, K., Serwicka, E.M.: Novel montmorillonite/TiO_2/MnAl-mixed oxide composites prepared from inverse microemulsions as combustion catalysts. Materials **10**(11), 1326 (2017)
69. Cheng, Z., Feng, B., Chen, Z., Zheng, J., Li, J., Zuo, S.: La_2O_3 modified silica-pillared clays supported PtO_x nanocrystalline catalysts for catalytic combustion of benzene. Chem. Eng. J. **392**, 123747 (2020)
70. Chen, Z., Li, J., Cheng, Z., Zuo, S.: Well-defined and highly stable AlNi composite pillared clay supported PdOx nanocrystal catalysts for catalytic combustion of benzene. Appl. Clay Sci. **163**, 227–234 (2018)
71. Attique, S., Batool, M., Goerke, O., Abbas, G., Saeed, F.A., Din, M.I., Jalees, I., Irfan, A., Gregory, D.H., Tufail Shah, A.: Fe-POM/attapulgite composite materials: efficient catalysts for plastic pyrolysis. Waste Manage. Res. **40**(9), 1433–1439 (2022)
72. Xing, X., Li, N., Cheng, J., Sun, Y., Wang, G., Zhang, Z., Xu, H., He, C., Hao, Z.: Hydrotalcite-derived $Cu_xMg_{3-x}AlO$ oxides for catalytic degradation of n-butylamine with low concentration NO and pollutant-destruction mechanism. Ind. Eng. Chem. Res. **58**(22), 9362–9371 (2019)
73. Ma, M., Jian, Y., Chen, C., He, C.: Spherical-like Pd/SiO_2 catalysts for n-butylamine efficient combustion: effect of support property and preparation method. Catal. Today **339**, 181–191 (2020)
74. Macías-Quiroga, I.F., Rengifo-Herrera, J.A., Arredondo-López, S.M., Marín-Flórez, A., Sanabria-González, N.R.: Research trends on pillared interlayered clays (PILCs) used as catalysts in environmental and chemical processes: bibliometric analysis. Sci. World J. **2022** (2022)

75. Henao-Aguirre, P.A., Macías-Quiroga, I.F., Giraldo-Gómez, G.I., Sanabria-González, N.R.: Catalytic oxidation of ponceau 4R in aqueous solution using iron-impregnated Al-pillared bentonite: optimization of the process. Bull. Chem. React. Eng. Catal. **16**(3), 491 (2021)
76. Guo, W., Hu, W., Pan, J., Zhou, H., Guan, W., Wang, X., Dai, J., Xu, L.: Selective adsorption and separation of BPA from aqueous solution using novel molecularly imprinted polymers based on kaolinite/Fe_3O_4 composites. Chem. Eng. J. **171**(2), 603–611 (2011)
77. Ziyat, H., Naciri Bennani, M., Hajjaj, H., Qabaqous, O., Arhzaf, S., Mekdad, S., Allaoui, S.: Adsorption of thymol onto natural clays of Morocco: kinetic and isotherm studies. J. Chem. **2020** (2020)
78. Gao, S., Wang, D., Huang, Z., Su, C., Chen, M., Lin, X.: Recyclable NiO/sepiolite as adsorbent to remove organic dye and its regeneration. Sci. Rep. **12**(1), 1–12 (2022)
79. Lou, Z., Zhou, Z., Zhang, W., Zhang, X., Hu, X., Liu, P., Zhang, H.: Magnetized bentonite by Fe_3O_4 nanoparticles treated as adsorbent for methylene blue removal from aqueous solution: synthesis, characterization, mechanism, kinetics and regeneration. J. Taiwan Inst. Chem. Eng. **49**, 199–205 (2015)
80. Lou, Z., Zhang, W., Hu, X., Zhang, H.: Synthesis of a novel functional group-bridged magnetized bentonite adsorbent: characterization, kinetics, isotherm, thermodynamics and regeneration. Chin. J. Chem. Eng. **25**(5), 587–594 (2017)
81. Rahmani, S., Zeynizadeh, B., Karami, S.: Removal of cationic methylene blue dye using magnetic and anionic-cationic modified montmorillonite: kinetic, isotherm and thermodynamic studies. Appl. Clay Sci. **184**, 105391 (2020)
82. Wang, N., Xiao, F., Zhang, J., Zhou, H., Qin, Y., Pan, D.: Spherical montmorillonite-supported nano-silver as a self-sedimentary catalyst for methylene blue removal. Appl. Clay Sci. **174**, 146–151 (2019)
83. Fei, F., Gao, Z., Wu, H., Wurendaodi, W., Zhao, S., Asuha, S.: Facile solid-state synthesis of Fe_3O_4/kaolinite nanocomposites for enhanced dye adsorption. J. Solid State Chem. **291**, 121655 (2020)
94. Oussalah, A., Boukerroui, A.: Alginate-bentonite beads for efficient adsorption of methylene blue dye Euro-Mediterranean. J. Environ. Integr. **5**(2). https://doi.org/10.1007/s41207-020-00165-z
85. Dai, H., Huang, Y., Huang, H.: Eco-friendly polyvinyl alcohol/carboxymethyl cellulose hydrogels reinforced with graphene oxide and bentonite for enhanced adsorption of methylene blue. Carbohyd. Polym. **185**, 1–11 (2018)
86. Jana, S., Ray, J., Mondal, B., Tripathy, T.: Efficient and selective removal of cationic organic dyes from their aqueous solutions by a nanocomposite hydrogel, katira gum-cl-poly (acrylic acid-co-N, N-dimethylacrylamide)@ bentonite. Appl. Clay Sci. **173**, 46–64 (2019)
87. Yang, Y., Yu, W., He, S., Yu, S., Chen, Y., Lu, L., Shu, Z., Cui, H., Zhang, Y., Jin, H.: Rapid adsorption of cationic dye-methylene blue on the modified montmorillonite/graphene oxide composites. Appl. Clay Sci. **168**, 304–311 (2019)
88. Munir, M., Saeed, M., Ahmad, M., Waseem, A., Sultana, S., Zafar, M., Srinivasan, G.R.: Optimization of novel Lepidium perfoliatum Linn. Biodiesel using zirconium-modified montmorillonite clay catalyst. Energy Sources, Part A: Recover., Util., Environ. Eff. **44**(3), 6632–6647 (2022)
89. Munir, M., Ahmad, M., Saeed, M., Waseem, A., Rehan, M., Nizami, A.S., Zafar, M., Arshad, M., Sultana, S.: Sustainable production of bioenergy from novel non-edible seed oil (Prunus cerasoides) using bimetallic impregnated montmorillonite clay catalyst. Renew. Sustain. Energy Rev. **109**, 321–332 (2019)
90. Shan, R., Shi, J., Yan, B., Chen, G., Yao, J., Liu, C.: Transesterification of palm oil to fatty acids methyl ester using K_2CO_3/palygorskite catalyst. Energy Convers. Manage. **116**, 142–149 (2016)
91. Munir, M., Ahmad, M., Rehan, M., Saeed, M., Lam, S.S., Nizami, A.S., Waseem, A., Sultana, S., Zafar, M.: Production of high quality biodiesel from novel non-edible Raphnus raphanistrum L. seed oil using copper modified montmorillonite clay catalyst. Environ. Res. **193**, 110398 (2021)

92. Naik, B.D., Meivelu, U.: Experimental studies on sodium methoxide supported bentonite catalyst for biodiesel preparation from waste sunflower oil. Environ. Prog. Sustain. Energy **39**(4), e13390 (2020)
93. Hamzah, N., Yusof, I., Samad, W.Z., Saleh, S.H., Ahmad Tajuddin, N., Ibrahim, M.L.: Production of biodiesel from waste cooking oil using bentonite catalysts. J. Acad. **9**, 139–144 (2021)
94. Đặng, T.H., Chen, B.H., Lee, D.J.: Optimization of biodiesel production from transesterification of triolein using zeolite LTA catalysts synthesized from kaolin clay. J. Taiwan Inst. Chem. Eng. **79**, 14–22 (2017)
95. Jalalmanesh, S., Kazemeini, M., Rahmani, M.H., Zehtab Salmasi, M.: Biodiesel production from sunflower oil using K_2CO_3 impregnated kaolin novel solid base catalyst. J. Am. Oil. Chem. Soc. **98**(6), 633–642 (2021)
96. Lycourghiotis, S., Kordouli, E., Kordulis, C., Bourikas, K.: Transformation of residual fatty raw materials into third generation green diesel over a nickel catalyst supported on mineral palygorskite. Renew. Energy **180**, 773–786 (2021)
97. Aslan, S., Aka, N., Karaoglu, M.H.: NaOH impregnated sepiolite based heterogeneous catalyst and its utilization for the production of biodiesel from canola oil. Energy Sources, Part A: Recover., Util., Environ. Eff. **41**(3), 290–297 (2019)
98. Silveira Jr., E.G., Justo, O.R., Perez, V.H., Reyero, I., Serrano-Lotina, A., Campos Ramirez, L., dos Santos Dias, D.F.: Extruded catalysts with magnetic properties for biodiesel production. Adv. Mater. Sci. Eng. **2018** (2018)
99. Tahir, M., Tahir, B.: 2D/2D/2D O-C3N4/Bt/Ti3C2Tx heterojunction with novel MXene/clay multi-electron mediator for stimulating photo-induced CO_2 reforming to CO and CH_4. Chem. Eng. J. **400**, 125868 (2020). https://doi.org/10.1016/j.cej.2020.125868
100. Chuaicham, C., Pawar, R.R., Karthikeyan, S., Ohtani, B., Sasaki, K.: Fabrication and characterization of ternary sepiolite/g-C_3N_4/Pd composites for improvement of photocatalytic degradation of ciprofloxacin under visible light irradiation. J. Colloid Interface Sci. **577**, 397–405 (2020)
101. Mishra, A., Mehta, A., Basu, S.: Clay supported TiO_2 nanoparticles for photocatalytic degradation of environmental pollutants: a review. J. Environ. Chem. Eng. **6**(5), 6088–6107 (2018)
102. Tahir, M.: Synergistic effect in MMT-dispersed Au/TiO_2 monolithic nanocatalyst for plasmon-absorption and metallic interband transitions dynamic CO_2 photo-reduction to CO. Appl. Catal. B **219**, 329–343 (2017)
103. Tahir, M.: Ni/MMT-promoted TiO_2 nanocatalyst for dynamic photocatalytic H_2 and hydrocarbons production from ethanol-water mixture under UV-light. Int. J. Hydrogen Energy **42**(47), 28309–28326 (2017)
104. Szczepanik, B.: Photocatalytic degradation of organic contaminants over clay-TiO_2 nanocomposites: a review. Appl. Clay Sci. **141**, 227–239 (2017)
105. Fajrina, N., Tahir, M.: 2D-MMT-dispersed g-C_3N_4/TiO_2 2D/0Dnanocomposite for enhanced photo-induced H_2 evolution from glycerol-water mixture. Appl. Surf. Sci. **471**, 1053–1064 (2019)
106. Valášková, M., Tokarský, J., Pavlovský, J., Prostějovský, T., Kočí, K.: α-Fe_2O_3 nanoparticles/vermiculite clay material: structural, optical and photocatalytic properties. Materials **12**(11), 1880. https://doi.org/10.3390/ma12111880
107. Lin, S., Zhang, Y., You, Y., Zeng, C., Xiao, X., Ma, T., Huang, H.: Bifunctional hydrogen production and storage on 0D–1D heterojunction of Cd0. 5Zn0. 5S@ Halloysites. Adv. Funct. Mater. **29**(39), 1903825 (2019). https://doi.org/10.1002/adfm.v29.39. https://doi.org/10.1002/adfm.201903825
108. Vinokurov, V.A., Stavitskaya, A.V., Chudakov, Y.A., Ivanov, E.V., Shrestha, L.K., Ariga, K.: Formation of metal clusters in halloysite clay nanotubes. Sci. Technol. Adv. Mater. **18**(1), 147–151 (2017). https://doi.org/10.1080/14686996.2016.1278352
109. Umer, M., Tahir, M., Azam, M.U., Tahir, B., Jaffar, M.M., Alias, H.: Montmorillonite dispersed single wall carbon nanotubes (SWCNTs)/TiO_2 heterojunction composite for enhanced

dynamic photocatalytic H_2 production under visible light. Appl. Clay Sci. **174**, 110–119. https://doi.org/10.1016/j.clay.2019.03.029

110. Umer, M., Tahir, M., Azam, M.U., Jaffar, M.M.: Metals free MWCNTs@TiO_2@MMT heterojunction composite with MMT as a mediator for fast charges separation towards visible light driven photocatalytic hydrogen evolution. Appl. Surf. Sci. **463**, 747–757 (2019)
111. Fajrina, N., Tahir, M.: Monolithic Ag-Mt dispersed Z-scheme pCN-TiO_2 heterojunction for dynamic photocatalytic H_2 evolution using liquid and gas phase photoreactors. Int. J Hydrogen Energy **45**(7), 4355–4375 (2020). https://doi.org/10.1016/j.ijhydene.2019.11.194
112. Liu, L., Chen, H., Shiko, E., Fan, X., Zhou, Y., Zhang, G., Luo, X., Hu, X.E.: Low-cost DETA impregnation of acid-activated sepiolite for CO_2 capture. Chem. Eng. J. **353**, 940–948 (2018). https://doi.org/10.1016/j.cej.2018.07.086
113. Barrett-Catton, E., Ross, M.L., Asuri, P.: Multifunctional hydrogel nanocomposites for biomedical applications. Polymers **13**(6), 856 (2021). https://doi.org/10.3390/polym13060856
114. Peña-Parás, L., Sánchez-Fernández, J.A., Vidaltamayo, R. (2018). Nanoclays for biomedical applications. In: Handbook of Ecomaterials, pp. 1–19. Springer International Publishing, Cham
115. Saikia, P.: Clay nanostructures for biomedical applications. In: Two-Dimensional Nanostructures for Biomedical Technology, pp. 137–172. Elsevier
116. Zhang, G., Wu, T., Lin, W., Tan, Y., Chen, R., Huang, Z., Yin, X., Qu, J.: Preparation of polymer/clay nanocomposites via melt intercalation under continuous elongation flow. Compos. Sci. Technol. **145**, 157–164 (2017). https://doi.org/10.1016/j.compscitech.2017.04.005

Environmental Applications of Natural and Surface-Modified Zeolite

Fazila Younas, Irshad Bibi, Amna Zulfqar, Muhammad Shahid, Muhammad Bilal Shakoor, Muhammad Mahroz Hussain, Nabeel Khan Niazi, and Muhammad Farrakh Nawaz

Abstract Zeolite is a natural crystalline aluminosilicate which is found naturally in the sedimentary rocks but can also be synthesized artificially under controlled conditions. In past few decades, natural zeolite and surface-modified zeolites (SMZs) have emerged as sustainable and environmental friendly materials which have numerous applications in cement manufacture (as stabilizer), soil amendment and wastewater treatment as well as adsorbent for remediation purpose. In the environment, there are various types of contaminants such as inorganic heavy metal (liod)s and organic compounds that have been proven threat not only to the humans but to the surrounding ecosystems. Considering the environmental threat, many approaches have been used, of which adsorption has been classified as safe and environmentally-friendly technique. Depending upon adsorption efficacy, zeolite-based materials are known to be safe for human being and environment. To date, various zeolitic-based materials have been used to detoxify heavy metals and other contaminants within in the environment. But due to limitation of research on zeolite application in the process of adsorption, the contaminant removal efficiency of zeolite is still unclear. Therefore, its application in the development of efficient, cost-effective and novel technologies for the

---

F. Younas · I. Bibi (✉) · A. Zulfqar · M. M. Hussain · N. K. Niazi
Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad,
Faisalabad 38040, Pakistan
e-mail: irshad.niazi81@gmail.com; irshad.niazi@uaf.edu.pk

N. K. Niazi
e-mail: nabeelkniazi@gmail.com

M. Shahid
Department of Environmental Sciences, COMSATS University Islamabad, Vehari Campus,
Vehari, Pakistan

M. B. Shakoor
College of Earth and Environmental Sciences, University of the Punjab, Lahore 54000, Pakistan

N. K. Niazi
Faculty of Engineering and Science, Southern Cross University, Lismore, NSW 2480, Australia

M. F. Nawaz
Institute of Environmental Studies, University of Karachi, Karachi 75270, Pakistan

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research
and Technology, https://doi.org/10.1007/978-981-99-2544-5_17

treatment of contaminated water, air, and soil is needed to be explored for contaminant remediation in water and soil systems. Zeolite application in remediation of the contaminated environments through adsorption-based techniques is believed to be the most effective, cheap, and sustainable way. In this chapter, various recent achievements of the potential application of natural zeolite and surface-modified zeolite for the removal of contaminants from contaminated soil and water are discussed. Also, sources and occurrence of zeolite will be elucidated. Moreover, the major research gaps and zeolites application as adsorbents will be discussed critically. Critical understanding of the zeolite behaviors under different environments will be explained briefly.

Keywords Adsorbent-based zeolite · Environmental applications · Sequestration and immobilization

1 Introduction

In addition to zeolite's widespread applications in the microelectronics, chemical industry, optics, and some other areas, it is also widely used for environmental protection. Its wide application includes its applicability in decontamination of wastewater and groundwater contaminated with organic and inorganic (heavy metal (liods) contaminant, carriers of herbicides, slow-release fertilizers, pesticides and fungicides production, improving carbon sequestration, acts as soil conditioners, also enhancing water holding capacity, and soil structure improving soil productivity [3, 8, 53, 55, 118]. Natural and synthetic zeolite have potential to remediate wastewater where it not only removes chromaticity and turbidity but also mitigate and detoxify heavy metal cations, ammonium, and other organic contaminants like xylene, benzene, and others. However, it is known that natural zeolite is very effective in removing cations such as phosphorus and heavy metal oxyanions [116].

Because of negatively charged surfaces, natural zeolites have been commonly used to remediate cationic contaminants in soil that prevents their leaching from soil profile like nitrates which causes many human health and environmental issues by entering water bodies [24]. Surface-modified zeolites (SMZs) can adsorb anions if it is modified with different species having positive charges to enable various anions adsorption [16, 88]. Mechanism of contaminants removal by low-cost sorbents is shown in Fig. 1.

The strong- and weak-base organic anion exchangers have been commonly used for zeolite modification and synthetic resins are often not more suitable because of their potential hazard to emerge as secondary contaminants, and artificial synthesized zeolite from natural materials is unstable under various soil conditions [18].

For more environmental-friendly applications, natural/synthetic zeolites are modified with metal oxides or metal cations in effective, simple, and relatively inexpensive processes [43]. The charged properties of modified zeolite based on the type of modifier and the manufacturing conditions [74]. Using various improved methods,

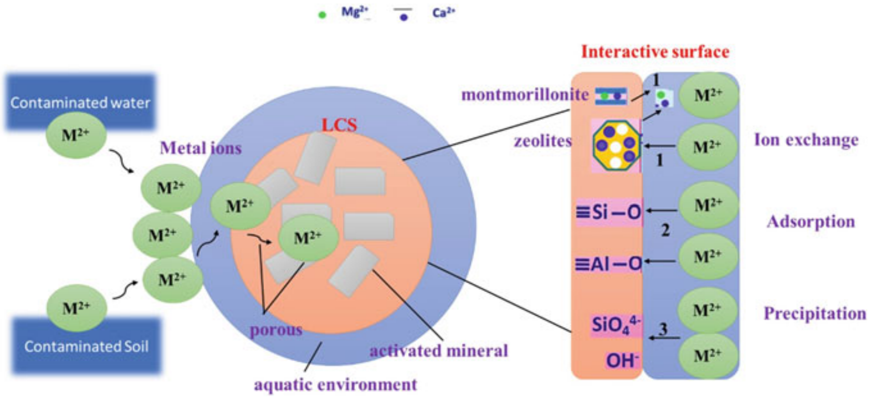


Fig. 1 Mechanism of heavy metal ions removal by low-cost sorbents (LCS) (modified from Chen and Shi [19])

efforts are being made to significantly increase the potential of zeolite surface adsorption. The use of modified zeolite to remove contaminants has attracted new research interest not only because of its remarkable appearance and performance, but also because of its optimized performance and low cost [31, 32, 112].

Recently, SMZs are mainly used for remediating contaminants from contaminated wastewater. However, to our knowledge no data has been published on natural and surface-modified zeolites to create an advance understanding on its mechanism and application in contaminants remediation. This chapter summarizes zeolite synthesis methods and its modification approaches. In general, this chapter will give people a critical understanding for the application of natural and SMZs in environmental remediation and offers broad perspectives for future applications. This chapter also discussed the major research gaps that must be needed to be filled for broad-spectrum application and enhanced efficiency of the zeolite (natural or SMZs) in sustainable environmental protection.

2 Background Study, Origin, Classification, and Critical Properties of the Zeolite Compounds

Generally, zeolites have diverse group of alkaline, inorganic, and hydrated-crystalline aluminum silicates. Its tetrahedral structure connects adjacent corners by sharing their oxygen atoms (*O*-positions), making a regular nonlinear arrangement of uniform cavities or channels cages of molecular proportions (typically in the 4–15 Å range) [39]. Internal skeleton of zeolite is form by three-dimensional framework of four-valent TO_4 unit cells (T = Al, Co, B, Ga, P, Fe, and Ge) accommodating a various quaternary ammonium cations or alkaline earth metal that's its empirical chemical derivation [39, 122, 132] is:

$$M_{x/n}[\mathrm{Al}_x\mathrm{Si}_y\mathrm{O}_{2(x+y)}]\cdot p\mathrm{H}_2\mathrm{O} \tag{1}$$

$M_{x/n}[\mathrm{Al}_x\mathrm{Si}_y\mathrm{O}_{2(x+y)}]\cdot\mathrm{pH}_2\mathrm{O}$ with M is (Ca, Mg, Ba, Sr) or (Na, K, Li), n is cation charge; $p/x = 1$–4, $y/x = 1$–6.

Zeolite has crystalline pentasil ring that exhibits high ion exchange capacity, unique hydrophilicity containing molecular sieve, large porous surface area, inherent charge balancing cations, flexible shape selectivity, and electrochemical behavior which enhance the high level of encapsulation network increasing adsorption affinity. Embedded silanol (Si–OH) (made by bond defects between oxygen and silicon atoms during crystal growth), Brönsted acid hydroxyl (bridging Si–OH–Al structure), and Lewis acid (from 2 it is made by dehydration) make its structure unique for encapsulation and adsorption. The acidic hydroxyl group in a vacuum of 750 K is characterized by its strong hydrogen bond, the induced dipole–dipole moment and the polarization attraction of the electrostatic interaction (π-electrons) [28, 87, 126].

Natural zeolite is primarily derived from a variety of ash, volcanic rock, biological silicon dioxide, quartz, and clay [35]. The main forms are clinoptilolite, mordenite, chabazite, analcime, erionite, chabazite, apatite, bauxite, laurel stone, limonite, sodium zeolite, sphalerite, limonite, paulownia, matzite, and barium iron ore that are deposited by sol–gel, microwave heating, centrifugation, redispersion, dip coating calcination, co-polycondensation, carbonization (polymer blends and organic aerogels), crystallization, templating, and hydrothermal treatments for commercial formation of zeolite modifications [34, 39, 59, 91]. Common zeolite was first discovered by Friedrich Axel Cronstedt in 1756 for the first time. Swedish mineralogists observed the warming of pyroxene and created the common name for zeolite using two Greek words (zein (cooking) and lithium (stone)). In the years 1862 and 1940s, Richard Barrer and St. Claire Deville of Imperial College London believe that the origin laboratory for zeolite was created under the synergistic effect of a strong salt solution at an extremely high temperature (170–270 °C) [29]. Robert Milton demonstrated the major effect of newly precipitated aluminosilicate gels in the United States which led to the formation of Type X, Type Y, and Type A zeolites in the late 1950s [39].

In addition, with the slow expansion of quaternary ammonium cations and the foaming of organic components, zeolites were developed in the early 1960s. Beta zeolite was invented in 1967, and the prototype zeolite ZSM-5 was invented in 1972 [39]. Since then, zeolite applications have been vigorously expanded and consolidated the multidisciplinary zeolite combination including structural and concrete finishing materials (reduced weight, chloride permeability, moderate water content, improved workability properties, breaking strength, and slow drying). Its application in electronics (electrocatalysis, redox process, optoelectronics, electronic isolators, photonics, fuel cell development, electrochemical double-layer capacitors and microelectronics), physics (micron level, cement, bone materials), chemistry (enantioselective separation, chemical sensors, aquarium filter additives, oxidation chemistry, water purification, gas separation and ion softening), engineering (soil treatment, detergent manufacturing, enhanced cumene cracking, process enhancement, alkane hydroisomerization, solar heat collection, aromatic alkylation, reform catalysis, adsorption refrigeration industry and nanotechnology) and biological (double-O implants, animal feed use, cancer treatment, medical oxygen treatment, childbirth and diarrhea treatment) are noticed from past few decades [28, 39, 49]. It is estimated that the annual formation/production of natural zeolite in the world is 4 million tons/year, which is 2.6 million tons for China's unprecedented industrialization construction. The basic classification is based on the source and level, the improved transmission properties or the topological system [34, 91].

3 Natural and Surface-Modified Zeolites

The Swedish geologist Alex Fredrik Cronstedt first discovered zeolite as a rock in 1756 [80], after copper mine sample collection he, observed a lot of steam release after heating [64, 102]. Zeolite word was first given to it after this heating was observed meaning 'boiling stone' [54]. Synthetic zeolite after its first synthesis attracts great market demand in 1960s, especially when petroleum industry used it for the purpose of catalytic cracking [54]. It was reported in 1970s, when it was discovered that synthetic zeolite could replace the phosphate compound in washing powder, synthetic zeolite market demands reached at its maximum again. The increased demand has intensified research interest on zeolites [102]. Although natural zeolite has been around for some time, large-scale zeolite deposits were not discovered until the mid-twentieth century. With the intensification of research on synthetic zeolites, it has been found that these inexpensive natural zeolites have properties similar to more expensive synthetic materials. With the market share of materials, research on natural zeolite has increased. There are now more than 50 natural zeolites registered [101].

Natural zeolites have the crystal-like structure composed of silicon (aluminum) and oxygen tetrahedral structure consisting of many tetrahedral to form a porous hydrated anionic structure [76, 132]. Zeolite has the ability to exchange cations in the structure and lose or accept water molecules [57]. The mechanism of natural zeolite to remove pollutants is as follows: (a) connected and ordered channels or within the crystal,(b) excessive negative charges on the zeolite framework can be replaced by divalent or monovalent cations (Mg^{2+}, Ca^{2+}, and Na^{+}, K^{+}) balance [41, 50].

Widiastuti et al. [133] reported that the natural zeolite had a good ammonium removal performance at 150-min with 3.0 mg/g adsorption capacity. In another study, Zanin et al. [138] potential to remediate heavy metals by using natural zeolite was explored and according to results recovery time of copper was 180 min with 96% removal rate. Chromium equilibrium time was 300 min, and removal rate was 85.1%. After 360 min, the iron removal rate can reach 95.4% [138]. Surface-modified zeolite can increase the adsorption potential under certain conditions, due to impurities SMZs pores causes agglomeration issues [58, 112].

The efficiency of zeolite sorption process is dependent upon adsorbents chemical and structural composition. Adsorption potential of zeolite also depends on silicon/aluminum ratio in the structure, cation nature, its concentration, and its availability.

Modification in natural zeolite structure can increase the potential to remediate the contaminant. Various organic and inorganic pollutant can be adsorbed more efficiently on zeolite crystal lattice by various modification with acids/base or with impregnation of different surfactants that usually are used to change the hydrophobicity and hydrophilicity potential of zeolite [132]. There are several methods of modification that are physical, chemical, biological, and composite modifications explained below [112].

3.1 Physical and Chemical Modification

Ultrasonic and thermal modifications are two important methods used for physical modification for zeolite. In thermal modification, muffle furnace or microwave heating is used to modify zeolite physically which increase its surface adsorption potential by reducing surface resistance of zeolite. Ultrasound approach is used to remove pollutants from the zeolite pore, thus enhancing its adsorption capacity [143]. Generally, the improvement of the muffle furnace is to provide high-temperature (200–600 °C) natural zeolites for 2–5 h in the muffle furnace. Temperature plays an important role in affecting zeolite adsorption potential as high temperature can also destroy the crystalline structure of zeolite reducing its adsorption potential [107].

Natural zeolite can be modified by using microwave heating in which microwave radiations are used where heating and time are two factors that can increase the zeolite adsorption capacity. Overheating for longer time can destroy the surface and crystal lattice of the natural zeolite resulted in destroyed structure and lower adsorption ability. Fahmy et al. [36] reported to use microwave-treated zeolites for removal of divalent cadmium ions from wastewater. Results showed that optimum time was 140 min for removing maximum cadmium at 0.25 g of zeolite dose in 25 mL of cadmium-contaminated wastewater. Another method of physical modification is the use of ultrasonic waves in which sound waves of different frequencies and strength increased the adsorption capacity. As it was reported by Wang et al. [130] that removal rate of ammonia was 86.9% by ultrasonic modification of natural zeolite for 40 min at 560 W. Natural zeolite can be modified chemically by using different concentration of cationic surfactants, rare elements addition, salts, acids, and bases to enhance adsorption capacity for different [112]. The mechanism and advantages or disadvantages of different physical and chemical modification are given in Table 1.

3.2 Composite Modification

Natural zeolite modification can also be done by combining several methods of modification under ambient conditions. This can be achieved in different ways of combining ultrasonic, heating, and chemical modification all together to achieve a better goal of adsorption using natural zeolite [112]. The contaminants removed by various modifications are shown in Table 2. Shorter reaction time and enhanced adsorption capacity can be achieved by modifying natural zeolite using the ultrasonic and salts that even can remove the impurities from the zeolite crystals and replace the larger radius cations which can increase its adsorption potential.

Table 1 Characteristics of physical and chemical modification

Methods	Mechanism	Contaminants	Advantages	Disadvantages	References
Ultrasonic	Elimination of impurities from channel; increase surface area	Ammonia	Good penetration; removal of impurities from channel	Inefficient; always combined with other methods	[144]
Microwave oven-heating	Elimination of impurities from channel; increase hole diameter; uniform pore size	Ammonia	Heating time saving; good penetration; high efficiency	Uneven heating because of moisture in the zeolite	[9]
Acid	H^+ replaces Ca^{2+} and Mg^{2+} in zeolite which have large diameter to increase specific surface area and microporosity	Ammonia, antimony (III), uranium (VI)	Simple and convenient, improving cations adsorption capacity	Low cation exchange capacity due to H^+ competition and dissolution of Sitetrahedra and free linkages	[78]
Alkali	a. Dissolve silicon reduce Si/Al from zeolite; make uniform pore size; b. electrostatic interaction and form covalent bonds	Organics, ammonia, manganese (II), lead (II), copper (II), cadmium (II)	Simple and convenient, improving the removal rate of cations	Destruction of crystal structure by poor concentration control, reduction in absorption rate	[4, 106]
Cationic surfactant	a. Anions adsorption and associated compounds formation; b. cations exchange; c. organics adsorption by hydrophobic alkyl chain	Tungstate, antimonate phosphorus, ammonia, copper (II), nickel, iron aniline, EDTA	Increase anion removal rate	More expensive than salt modification. Complicated modification process	[56, 135]

(continued)

Table 1 (continued)

Methods	Mechanism	Contaminants	Advantages	Disadvantages	References
Salt	a. Exchanging with Ca^{2+} and Mg^{2+} in the zeolite, increasing the pore size; b. ligand-exchange and electrostatic interaction	Ammonia, iron (II), calcium (II), magnesium (II), manganese (II), copper (II), zinc (II), nickel (II), uranium (VI) phosphorus, fluoride, chromium (VI), arsenic (III), arsenic (V), lead (II)	High pollutants removal efficiency	Expensive salt solutions	[7, 73]

Wang et al. [130] showed that NaCl at 0.8 mol/L and ultrasonic waves with 560 W reduced the reaction time to 40 min, and removal efficiency reached 91.1% for ammonia. With ultrasonic and salts modifications, it can reduce the reaction time to 10 min, while natural zeolite has 60 min reaction time for ammonia. Two possible mechanism can be adopted for zeolite modifications, i.e., either by heating it first and then impregnation with different salts or methods. Other is first to modify it with different salts then heat it, this method is more efficient, and this modification allows better adsorption rate and lower reaction time.

Yang et al. [136] observed that NaOH (1.0 mol/L) and NaCl (2.0 mol/L) were used to treat the zeolite for 2 h and then this solution was heated for 0.5 h at 400 °C the removal efficiency increased remarkably from 54.5 to 98.3% for ammonia. This only took 140 min to reach equilibrium, according to kinetic curve for adsorption. In recent years, the modification of alkali/acid/salt complexes has also been investigated. Modifying zeolite compounds can shorten the adsorption time. Dionisiou et al. [31] reported that zeolite treated with HCl (1 M) for 24 h at 60 °C and then again mixing of HDTMA-Br (0.05 M) at 25 °C for 24 h can enhance boron adsorption. They concluded that boron efficiency reached up to 85% at pH 3.

4 Zeolites Applications

The diversity of the zeolite structure is caused by the change in pore size (between 2 and 13 A°). The change in shape and the network connection with 4–12 rings make zeolite one of the useful substances in various applications [6, 110]. Zeolite has a wide range of technical, industrial, agricultural, commercial, and biomedical uses. Hence, zeolite is called “magic stone” [60]. Synthetic zeolite is mainly used

Table 2 Removal of contaminants before and after zeolite modification

Modification method	Modifier (mol L^{-1})	Adsorbate (mg/L)	Zeolite			References
			Dosage (g L^{-1})	RBM (mg g^{-1})	IRAM (times)	
Salt	$MgCl_2$ (8.85)	Cu (II) (10.0)	2.0	1.90	1.11	[22]
Salt	$LaCl_3$ (0.163) NaCl (0.34) + $AgNO_3$ (0.012)	TP (5)	5.0	0.05	18.25 1.50	[69]
Alkali + salt	KOH (5.0) + $FeCl_3$ (3.0)	Zn (II) (3.0)	2.0	0.06	2.71	[79]
Salt	$MgCl_2$ (8.85)	Pb (II) (10.0)	2.0	3.30	0.36	[22]
Salt	NaCl (0.1) + $AlCl_3$ (0.1)	TP (25)	4.0	0.60	10.67	[44]
Alkali + salt	KOH (5.0) + $FeCl_3$ (3.0)	Pb (II) (3.0)	2.0	0.16	1.32	[79]
Salt	LDHs (0.1)	TP (32)	100	0.03	4.67	[46]
Salt	$MgCl_2$ (8.85)	Cd (II) (10.0)	2.0	2.30	0.87	[22]
Salt	$FeCl_3$ (3.5)	TP (50)	100	0.04	3.80	[99]
Alkali + salt	KOH (5.0) + $FeCl_3$ (3.0)	Cd (II) (3.0)	2.0	0.01	13.00	[79]
Microwave (476 W) + salt	NaCl (1.0)	TP (57)	80	0.13	1.65	[17]
Salt	MgAl-LDHs (1.0) MgFe-LDHs (2.0)	Cr (VI) (32)	50	0.03	1.03 0.27	[139]
Microwave (476 W) + salt	NaCl (1.0)	$NH^+{}_4$-N (389)	80	1.34	2.23	[17]
Salt	NaCl (1.0)	$NH^+{}_4$-N (120)	8.00	0.01	1.00	[67]
Ultrasonic + salt	NaCl (0.6)	$NH^+{}_4$-N (10)	2.5	0.34	9.66	[131]
Salt	$LaCl_3$ (0.163) NaCl (0.34) + $AgNO_3$ (0.012)	$NH^+{}_4$-N (20)	5.0	2.54	0.55 0.51	[69]

in industry. On the other hand, the price of natural zeolite is lower compared to synthetic zeolite, which leads to the fact that synthetic zeolite is replaced by natural zeolite, thus paving the way for its development in the market [6]. So far, natural zeolite has been used as a filler in the cement industry [12]. Clinoptilolite is used in agriculture as a potassium releasing agent and has a longer soil water holding capacity due to its good absorption properties [94]. In addition, natural zeolite is used for wastewater treatment and removal of soluble heavy metals [45]. Now a days, the detergent industry has developed a large number of zeolites due to its application and efficiency [110].

Zeolite is one of the effective catalysts for many organic reactions, has a variety of structures to accelerate chemical reactions, and is used as an absorbent and desiccant. Many gasoline and petrochemical products around the world are made using zeolite catalysts. One of the great interests of zeolite applications is biosensors. In recent years, research has been focused on use of zeolite-based materials to protect the environment [110]. This chapter introduces the different areas of zeolite in environmental remediation and its use to improve soil and water quality.

4.1 Application Efficiency of Natural Zeolite for Environmental Remediation

Natural zeolite use for the remediation of environment mainly depends on its ion exchange characteristics [11, 80]. Natural zeolite has only the ability to remove cation through ion exchange, but surface modification can enable to remediate anions too. Many factors can affect the metals cations adsorption rate like pH, competing cations, temperature, external surface activity, hydrated solutes concentration, and complexation with agents [26].

Thermodynamic and experimental studies have shown that zeolite is selective for monovalent ions, especially Cs^+ and $NH_4{}^+$. Zeolite has a much lower selectivity for divalent cations (like Pb^{2+}, Sr^{2+}) [15]. In several cases, multi-component adsorption experiments and thermodynamic calculations were carried out [90]. Due to the complexity of the composition of natural zeolite materials (such as the presence of other phases of adsorption, changes in zeolite content, etc.), the thermodynamic calculation of natural zeolite materials is not always that simple. The absorption of transition elements by natural zeolite is highly dependent on their water chemistry and hydrolysis reaction, producing various insoluble and soluble products which have some interaction with zeolite. In these conditions, the absorption mechanism includes not only adsorption and ion exchange/absorption but also co-precipitation/surface precipitation [80].

Materials with higher adsorption capacity were required for treating nuclear waste. Many patents relating to the application of zeolite derivatives (clinoptilolite) to immobilized radioactive cesium (Cs) isotopes appeared around 1960 [80]. Natural zeolite is used to limit the consequences of the nuclear accidents on Three Mile Island and

Chernobyl, to remove Cs and strontium (Sr) isotopes from wastewater produced from nuclear industry to purify the contaminated water [13, 123]. It's worth noting that the zeolite (Clinoptilolite) used in the wastewater plant has reduced or removed the Sr and Cs produced in the Sea of Irish to a constant lower concentration since it was commissioned in 1985 radiation conditions in the heavily contaminated area in this state greatly improved. It is also suggested that areas rich in natural zeolite (such as the Yucca Mountains in Nevada, USA) could be used as potential nuclear waste disposal sites [123].

The removal of heavy metals (e.g., Fe, Pb, Cd, Zn) from the drainage of acid mines is another area of potential environmental applications of natural zeolite materials [82]. In some cases, the regeneration of zeolite by various solutions has also been studied. When used material was zinc, the following desorption efficiency levels were observed: EDTA > NaCl > NaOAc > $NaHCO_3$ > NaOH > $Ca(OH)_2$.

Many studies recently published in the literature aim to remove or stabilize heavy metals, particularly Pb, in environmental matrices. Li et al. [66] reported to stabilize lead, cadmium, and nickel using zeolites successfully. Compared with the addition of single zeolite, the mixed treatment of artificially lead-contaminated garden soil (zeolite and humic acid) led to a higher removal of Pb levels in vegetative parts, while the water-soluble ratio of Pb compounds in the soil increased slightly [113]. Research and field tests on a laboratory scale have shown that natural zeolite and its modified forms lower the heavy metals concentration and contaminants in crops and are of environmentally importance on the barren land caused by vegetation restoration and metal pollution, which also limits soil erosion [61].

Clinoptilolite has been studied as an adsorbent for lithium (Li) to protect poplar vegetation growing in the soil that was contaminated. The Li was chosen as the main heavy metal because nuclear magnetic resonance can be used to trace Li directly [48]. Studies with Naples Yellow Tuff (NYT) to reduce the copper (Cu), lead (Pb), and zinc (Zn) toxicity of the soil to organisms that showed the presence of zeolite restores the friendliness of the soil environment of the biota by successfully restoring a large amount of fertilization. It is vitality, and at the same time, significantly reduces pathology and mortality [14].

The technical application of natural zeolite/organic mixtures and their synergistic effects on remediation are continuous and will become more important research in coming era [61]. Although there is only few information available in the literature reviews on the possible drawbacks of long-term use of zeolites which are naturally present in the world [80].

Water treatment and urban and industrial wastewater treatment are major areas of application with natural zeolite compounds [38, 100, 134]. The main investigated zeolite is natural zeolite used as adsorbent for NH_4^+ from urban and other contaminants originating from industrial wastewaters. Sewage and wastewater treatment plants using natural zeolite have been put into many processing globally. The reduction of many metals or nutrients (e.g. $H_2PO_4^2/HPO_4^-$, NH_4^+) recovery and quantitative precipitation in the slow-release fertilizer (SRF) were also recorded [80].

Some researchers have also considered using natural zeolite materials to reduce contaminants in highway rainwater [93]. In particular, the effectiveness of mixed materials (zeolite + vermiculite, zeolite + lava, and limestone) was examined [80]. Natural zeolite use in the treatment of brine/soda coal bed natural gas (CBNG) generated water has been investigated. For this reason, the calcium-rich natural zeolite was investigated as a potential Na adsorbent from CBNG water. Column tests have shown that one ton (1000 kg) of St. Cloud and Brazilian zeolite can be used to treat 16,000 and 60,000 L of CBNG water, respectively, to reduce the rate of sodium adsorption [141]. There are also attempts to reduce Na in seawater by using naturally produced zeolite and to reduce Cl with calcined hydrotalcite for agricultural purpose [125]. Finally, ferrite and mechanically activated natural zeolite materials were investigated as potential materials for specific environmental applications [80, 121].

4.2 Application Efficiency of Surface-Modified Zeolite for Environmental Remediation

A particularly main class of surface modification zeolite minerals for environmental remediation is zeolites used with surfactants. Combined with the improved cation adsorption characteristics of natural zeolite and the capacity to adsorb negative substances, pathogens, and non-polar organic substances from water currents, these materials are considered to be floor and water basin washers, backfill, and sealing materials when storing waste. It also acts as a barrier against the osmotic reaction of clean water. The most common modifiers are quaternary amines such as N-cetylpyridinium, HDTMA, and ODTMA that form a double-layer structure on the zeolite surface and thereby change their charge from negative to positive [27]. The positive surface charge provides a site for the adsorption of anions, and the organic-rich surface layer provides a distribution medium for the adsorption of non-polar organic compounds. The original cation exchange capacity of zeolite is also partially retained (Fig. 2).

Previous studies have explored the zeolite ability to bind metal anions like arsenate, chromate, and many others [42, 62]. Similar adsorption properties and capacities have been reported for zeolites which are modified with polymer [81, 86]. The production of modified zero-valent Fe-mixed particles with surfactant offers the reason of removing contaminants through combined reduction/adsorption [68]. Adsorption capacities of modified zeolite for different contaminants are shown in Table 3.

It has been found that natural zeolite modified with surfactants can effectively treat oilfield wastewater and adsorb volatile petroleum hydrocarbons [109]. The column regeneration method by air injection has also been investigated [2]. Modified-zeolite particles are excellent carriers of bacteria and can enhance the sludge activity of sewage treatment plants. The modification of zeolite with cationically active polyelectrolyte can promote interaction between bacteria and the surface of zeolite,

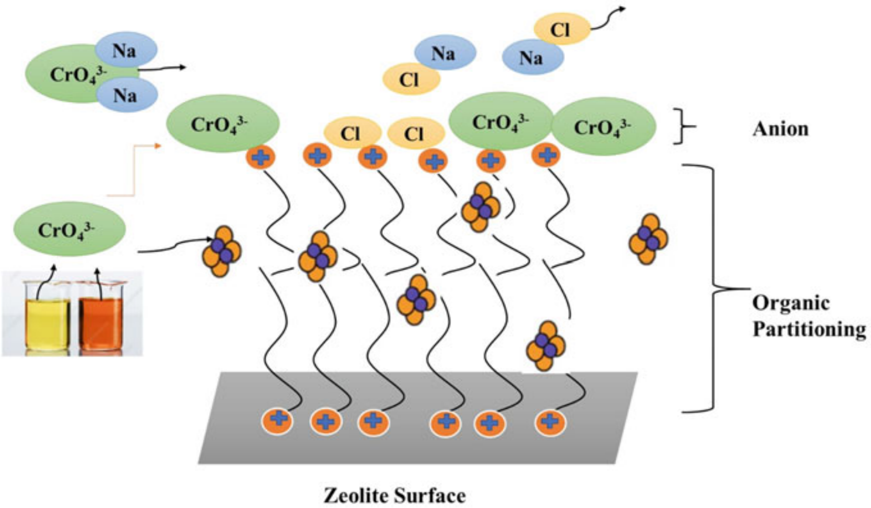


Fig. 2 Partitioning of a mixture of toxic chromate anions and perchloroethylene during their combined sorption by a surfactant-modified zeolite (SMZ) (modified from Rhodes [105])

whereby the sludge activity is further improved [96]. Zeolites modified with surfactants also showed the capacity to attach pathogens (such as *E. coli*) in wastewater [6, 108].

5 Sustainable Utilization of Natural and Surface-Modified Zeolite

It is estimated that the world production of natural zeolite in 2018 was 1.1 million tons, of which 120 kt were in South Korea, 300 kt in China, 100 kt in New Zealand, 20 kt in Jordan, and 95 kt and 70 kt in the United States and Turkey, respectively. Cuba is 57 kt and the total production of all other countries is 350 kt [120]. Zeolite costs about $ 100–150/ton in china and many researchers have been doing research on it due to its rich pore structure and they use it as filter media [129]. Organic and inorganic pollutant can be remediated with the help of zeolite application most importantly its role in remediating the fluoride ions from waste and drinking water is an new aspect of its application [142, 145]. Adsorption of heavy metal ions on various natural zeolites is shown in Table 4.

Zeolite as a substrate for constructed wetlands (CWs) has advantages of low cost and enhanced efficient wastewater treatment [1]. However, natural zeolite application is very extensive, but it has limited natural reserves, and its long-term application can exhaust the natural resources of zeolite. Limited use, modification, and regeneration of zeolite can enhance its efficiency, and it is also of great importance for sustainable

Table 3 Adsorption capacity of modified zeolite for different contaminants

Salt	Contaminants	Adsorbent capacity (mg/g)	Temperature (°C)	pH	Adsorption isotherm	References
NaCl	NH_4-N	11.3	25	8.0	Langmuir	[21]
NaCl	Manganese	10.0	25		Langmuir	[5]
NH_4Cl	Uranium	2.1	25	3.0	Langmuir	[10]
NH_4Cl	Manganese	24.3	25		Freundlich	[5]
$Al_2(SO_4)_3$	Manganese	25.1	25		Freundlich	[5]
DAAO	Anionic dye congo red	69.9–58.8	20–40	6.0	Langmuir	[71]
SDS	NOM	111.2	25	5.0	Langmuir	[75]
HDTMA	As EDTA Cr Phosphorus	1.6 159.8 5.2 0.2	23 25 25 25 ± 1	7.0 7.5 6.0 6.9	Freundlich Freundlich Langmuir Langmuir	[23] [56] [63] [33]
CPB	Tannic acid	111.0	30	5.5	Langmuir	[70]
CTMAB	Sodium dodecyl benzene sulfonate Pb	18.5 3.3	25 35	6.0	Langmuir Langmuir	[117] [103]
Ultrasonic composite	Ammonia	12.8	25		Langmuir	[131]
Heating composite	Ammonia	6.6	30		Langmuir	[68]
	Fluoride	2.6	25	8.0	Freundlich	[124]
	Bisphenol	16.5	25		Freundlich	[128]
Alkali acid/salt composite	Cr	6.3	25		Freundlich	[114]

use and development of zeolite. Synthetic zeolite can also reduce the pressure on the natural reserves of zeolite [127].

Zeolite regeneration and reproducibility is an important phenomena for its vast application [77]. Zeolite can be regenerated by following biological, chemical, and physical regeneration methods, and among these, biological method is mostly used [111]. Relevant studies have shown that using natural zeolite as a matrix of chemical waste through biological regeneration technology has low cost and good effect. In-situ bioremediation technology, which combines microbial metabolism and ion exchange, offers the advantages of ease of use and low processing costs [20, 47]. Zeolite application in different biological treatment process including CWs is beneficial for attaining high efficiencies. The biological regeneration technology has the shortcomings of long cycle and low efficiency, so further research is required.

Modified zeolite is a most important method that helps to enhance the cleaning effect of zeolite as a continuous water matrix and to extend the usage time of zeolite.

Table 4 Adsorption of heavy metal ions on various natural zeolites

Material	Metal	Adsorption (meq/g)	References
Turkish clinoptilolite	Pb^{2+} Zn^{2+} Cu^{2+} Ni^{2+}	0.299–0.730 0.108–0.251 0.022–0.227 0.017–0.173	[89]
Clinoptilolite	Cd^{2+}	0.12–0.18	[40]
Mexican clinoptilolite	Pb^{2+}	1.4	[72]
Sardinian clinoptilolite	Cu^{2+} Cd^{2+} Pb^{2+} Zn^{2+}	0.34 0.05–0.19 0.27–1.2 0.1	[25]
Ukraine clinoptilolite	Pb^{2+} Cu^{2+} Ni^{2+} Cd^{2+}	0.134 0.405 0.222 0.0375	[115]
Natural modified zeolite	Cd^{2+} Cr^{6+} Cu^{2+} Zn^{2+}	$Cd^{2+} > Cu^{2+} > Cr^{6+} > Zn^{2+}$	[92]
Penggunaan zeolite	Cd^{2+}	2.39 mg/g	[95]
Pemanfaatan zeolite	Fe^{3+} Cr^{6+}	36.9% for Fe^{3+} 68.05 for Cr^{6+}	[104]
Natural zeolite	Cr^{6+}	4.365 mg/g	[84]
Natural zeolite	Hg^{2+}	2.5 mg/g	[83]
Natural zeolite	Pb^{2+}	52 mg/g	[97]
Natural zeolite	Pb^{2+}	72 mg/g	[98]

The important surface modification methods are alkali treatment, acid treatment, ion exchange, microwave treatment, heat treatment, and surface modification [119]. The thermal modification consists of heating zeolite to remove water and organic waste by increasing surface area and improve its adsorption and ion exchange capabilities. The acid modification consists in dissolving impurities in zeolite structure with mineral acid, opening pores, and improving surface of zeolite lattice [145]. The modification with inorganic salt consists in replacing Mg^{2+} and Ca^{2+} plasma in zeolite structure and enhancing adsorption site to increase the surface area and the ion exchange capacity. The modified zeolite with LDH membrane increases the adsorption-active sites, enriches the pore structure, and strengthens adsorption [46]. After the zeolite is modified, the Si/Al ratio decreases, the porosity increases, the surface activity increases, and the adsorption and ion exchange performance improves [127]. From a mechanical point of view, the improved process also promotes the regeneration and use of zeolite and realizes the sustainable use of zeolite.

It has been found that the cost of using magnesium salt modified natural zeolite for wastewater treatment has increased by more than 60%. The cost of zeolite modification is mainly attributed to the cost of most modifiers. The use of heating and ultrasound technology, as well as water usage and equipment depreciation, make up a percentage of the cost. Modification cost of zeolite by using NaCl is much lower than other salts [52]. Although the total phosphorus (TP) removal rate of alum sludge using the LDHs modifier has been greatly improved in the water supply system and waste is used, the complex manufacturing process increases the modification cost. The TP removal rate has been significantly improved. The use of waste in the water supply system and the complex manufacturing process have increased transformation costs [46]. Commercial acids and alkali application may also reduce the zeolite modification [37]. Heat generation by using waste also reduces the cost of zeolite modification.

The manufacture of synthetic zeolite is very important to relieve the pressure on the use of natural zeolite. Using waste as a raw material can effectively reduce the cost of synthetic zeolites. Waste currently used includes fly ash, silica vapor waste, red mud, coal dam, blast furnace slag, and petroleum reserves [30, 65, 127]. Only China produced 540 million tons of fly ash in 2015 due to its abundant resources [140]. The content of Al_2O_3 and SiO_2 in fly ash is up to 80%, which has strong adsorption and wide application prospects in the synthesis of zeolite. Although some solid wastes are used to make zeolite for resource use, it is difficult to make high purity zeolite because of the high levels of impurities in the raw materials. At present, the process of synthesizing zeolite is complicated, expensive, and difficult to mine [27]. It is also necessary to simplify the process flow, reduce production costs, improve the purity of zeolite products, and realize the sustainable use of zeolite.

6 Cost Estimation of Zeolites

Zeolite due to its low cost makes it more efficient to use for remediation process. Cost benefit and adsorption capacity are two most critical factors to be consider for a good adsorbent. But the adsorbent potential can vary with the several factors like competition between the pollutants, initial concentration, pH and most importantly, the analytical method which was adopted, i.e., incubation, sorption, column, and kinetic sorption isotherms [51].

As mentioned above, one of the most popular adsorbents used in wastewater treatment is zeolite. In Korea, the price of natural zeolite is usually 1.6 ± 0.5 USD/kg [85]. In China, natural zeolite is very cheap at around US $ 140 per cubic meter (particle size: 1 mm). However, there are few reports of the cost of using modified zeolites to remove impurities. Most of the articles only describe batch trials as the cost depends largely on many factors, such as the availability of raw materials, the processing required, the modification methods, and the processing conditions [51]. In addition, inconsistent data presentation makes it difficult to compare different adsorbents/modification methods.

7 Conclusion and Future Perspective

This chapter briefly introduced the modification methods of zeolite with physical, chemical, and composite modification. Various methods for improving the adsorption potential of zeolite on various contaminants in wastewater have also been explored. Over the years, the industrialization and global growth of the world have gradually increased, moving towards the generation of large amounts of waste. Projections for the next 20 years suggest that industrial manufacturing will fail and then generate a large amount of waste. Today, the increasingly profound differences in field applications and the limited success of repairs have led people to recognize the use of natural zeolite or modified zeolite as a control environment.

Acknowledgements The authors are thankful to Higher Education Commission (Project Nos. 6425/Punjab/NRPU/R&D/HEC/2016 and 6396/Punjab/NRPU/R&D/HEC/2016), Pakistan for providing financial support. Drs. Nabeel Khan Niazi and Irshad Bibi are thankful to the University of Agriculture Faisalabad. Dr. Irshad Bibi acknowledges the support form COMSTEQ-TWAS research grant 2018 (18-268 RG/EAS/AS_C).

References

1. Al Dwairi, R., Omar, W., Al-Harahsheh, S.: Kinetic modelling for heavy metal adsorption using Jordanian low cost natural zeolite (fixed bed column study). J. Water Reuse Desalination **5**, 231–238 (2015)
2. Altare, C.R., Bowman, R.S., Katz, L.E., Kinney, K.A., Sullivan, E.J.: Regeneration and long-term stability of surfactant-modified zeolite for removal of volatile organic compounds from produced water. Microporous Mesoporous Mater. **105**, 305–316 (2007)
3. Aminiyan, M.M., Sinegani, A.A.S., Sheklabadi, M.: Aggregation stability and organic carbon fraction in a soil amended with some plant residues, nanozeolite, and natural zeolite. Int. J. Recycl. Org. Waste Agric. **4**, 11–22 (2015)
4. Ates, A., Akgül, G.: Modification of natural zeolite with NaOH for removal of manganese in drinking water. Powder Technol. **287**, 285–291 (2016)
5. Ates, A.: Role of modification of natural zeolite in removal of manganese from aqueous solutions. Powder Technol.**264**, 86–95 (2014)
6. Auerbach, S.M., Carrado, K.A., Dutta, P.K.: Handbook of Zeolite Science and Technology. CRC Press (2003)
7. Awuah, J.B., Dzade, N.Y., Tia, R., Adei, E., Kwakye-Awuah, B., Catlow, C.R.A., de Leeuw, N.H.: A density functional theory study of arsenic immobilization by the Al (III)-modified zeolite clinoptilolite. Phys. Chem. Chem. Phys. **18**, 11297–11305 (2016)
8. Azough, A., Marashi, S.K., Babaeinejad, T.: Growth characteristics and response of wheat to cadmium, nickel and magnesium sorption affected by zeolite in soil polluted with armaments. J. Adv. Environ. Health Res. **5**, 163–171 (2017)
9. Bagheri, S., Hir, Z.A.M., Yousefi, A.T., Hamid, S.B.A.: Progress on mesoporous titanium dioxide: synthesis, modification and applications. Microporous Mesoporous Mater. **218**, 206–222 (2015)
10. Bakatula, E.N., Mosai, A.K., Tutu, H.: Removal of uranium from aqueous solutions using ammonium-modified zeolite. S. Afr. J. Chem.**68**, 165–171 (2015)
11. Belviso, C.: Zeolite for potential toxic metal uptake from contaminated soil: a brief review. Processes **8**, 820 (2020)

12. Bilim, C.: Properties of cement mortars containing clinoptilolite as a supplementary cementitious material. Constr. Build. Mater., 3175–3180 (2011)
13. Borai, E., Harjula, R., Paajanen, A.: Efficient removal of cesium from low-level radioactive liquid waste using natural and impregnated zeolite minerals. J. Hazard. Mater. **172**, 416–422 (2009)
14. Buondonno, A., Coppola, E., de Nicola, E., Colella, C.: Zeolitized tuffs in restorative pedotechnical activities: evidence of soil toxicity abatement against biota through bio-test with sea urchin Paracentrotus lividus. In: Studies in Surface Science and Catalysis, vol. 158, pp. 2057–2064. Elsevier (2005)
15. Caputo, D., Pepe, F.: Experiments and data processing of ion exchange equilibria involving Italian natural zeolites: a review. Microporous Mesoporous Mater. **105**, 222–231 (2007)
16. Castillo, J.M., Silvestre-Albero, J., Rodriguez-Reinoso, F., Vlugt, T.J., Calero, S.: Water adsorption in hydrophilic zeolites: experiment and simulation. Phys. Chem. Chem. Phys. **15**, 17374–17382 (2013)
17. Chang, C., Xing, Z., Chen, Y.: Treatment of biogas slurry with microwave-NaCl modified zeolite. JoNA, Ed. FU-NS**42**, 218–222 (2014)
18. Chatterjee, S., Lee, D.S., Lee, M.W., Woo, S.H.: Nitrate removal from aqueous solutions by cross-linked chitosan beads conditioned with sodium bisulfate. J. Hazard. Mater. **166**, 508–513 (2009)
19. Chen, G., Shi, L.: Removal of Cd (II) and Pb (II) ions from natural water using a low-cost synthetic mineral: behavior and mechanisms. RSC Adv., 43445–43454 (2017)
20. Chen, J., Wang, X., Zhou, S., Chen, X., Wang, Y.: Adsorption and in-situ regeneration of bio-zeolite for treatment of low temperature wastewater containing ammonia-nitrogen. Technol. Water Treat. **45**, 92–96 (2019)
21. Cheng, Q., Li, H., Xu, Y., Chen, S., Liao, Y., Deng, F., Li, J.: Study on the adsorption of nitrogen and phosphorus from biogas slurry by NaCl-modified zeolite. PLoS ONE**12**, e0176109 (2017)
22. Choi, H.-J., Yu, S.-W., Kim, K.H.: Efficient use of Mg-modified zeolite in the treatment of aqueous solution contaminated with heavy metal toxic ions. J. Taiwan Inst. Chem. Eng.**63**, 482–489 (2016)
23. Chutia, P., Kato, S., Kojima, T., Satokawa, S.: Adsorption of As (V) on surfactant-modified natural zeolites. J. Hazard. Mater. **162**, 204–211 (2009)
24. Cieśla, J., Franus, W., Franus, M., Kedziora, K., Gluszczyk, J., Szerement, J., Jozefaciuk, G.: Environmental-friendly modifications of zeolite to increase its sorption and anion exchange properties, physicochemical studies of the modified materials. Mater. (Basel, Switz.) **12**, 3213 (2019)
25. Cincotti, A., Mameli, A., Locci, A.M., Orrù, R., Cao, G.: Heavy metals uptake by Sardinian natural zeolites: experiment and modeling. Ind. Eng. Chem. Res.**45**, 1074–1084 (2006)
26. Colella, C.: Recent advances in natural zeolite applications based on external surface interaction with cations and molecules. Stud. Surf. Sci. Catal. **170**, 2063–2073 (2007)
27. Collins, F., Rozhkovskaya, A., Outram, J.G., Millar, G.J.: A critical review of waste resources, synthesis, and applications for zeolite LTA. Microporous Mesoporous Mater. **291**, 109667 (2020)
28. Coronas, J.: Present and future synthesis challenges for zeolites. Chem. Eng. J. **156**, 236–242 (2010)
29. Cundy, C.S., Cox, P.A.: The hydrothermal synthesis of zeolites: precursors, intermediates and reaction mechanism. Microporous Mesoporous Mater. **82**, 1–78 (2005)
30. Czuma, N., Casanova, I., Baran, P., Szczurowski, J., Zarębska, K.: CO_2 sorption and regeneration properties of fly ash zeolites synthesized with the use of differentiated methods. Sci. Rep. **10**, 1–9 (2020)
31. Dionisiou, N.S., Matsi, T., Misopolinos, N.D.: Removal of boron by surfactant modified zeolitic tuff from northeastern Greece. J. Agric. Sci. **5**, 94 (2013)
32. Dionisiou, N.S., Matsi, T., Misopolinos, ND.: Phosphorus adsorption–desorption on a surfactant-modified natural zeolite: a laboratory study. Water Air Soil Pollut. **224**, 1–10 (2013)

33. Dionisiou, N.S., Matsi, T., Misopolinos, N.D.: Phosphorus adsorption–desorption on a surfactant-modified natural zeolite: a laboratory study. Water, Air, Soil Pollut. **224**, 1–10 (2013)
34. Egeblad, K., Christensen, C.H., Kustova, M., Christensen, C.H.: Templating mesoporous zeolites. Chem. Mater. **20**, 946–960 (2008)
35. Erdős, M., Geerdink, D.F., Martin-Calvo, A., Pidko, E.A., van den Broeke, L.J., Calero, S., Vlugt, T.J., Moultos, O.A.: In silico screening of zeolites for high-pressure hydrogen drying. ACS Appl. Mater. Interfaces (2021)
36. Fahmy, A., Youssef, H., Elzaref, A.: Adsorption of cadmium ions onto zeolite-A prepared from Egyptian kaolin using microwave. Int. J. Sci. Res. **5**, 1549–1555 (2016)
37. Ferreira, A.S., Mansur, M.B.: Statistical analysis of the spray roasting operation for the production of high quality Fe_2O_3 from steel pickling liquors. Process Saf. Environ. Prot. **89**, 172–178 (2011)
38. Filippidis, A., Apostolidis, N., Filippidis, S., Paragios, I.: Purification of industrial and urban wastewaters, production of odorless and cohesive zeo-sewage sludge using Hellenic Natural Zeolite. In: Proceedings, Second International Conference on Small and Decentralized Water and Wastewater Treatment Plants, pp. 403–408 (2008)
39. Foo, K.Y., Hameed, B.H.: The environmental applications of activated carbon/zeolite composite materials. Adv. Colloid Interface Sci. **162**, 22–28 (2011)
40. Gedik, K., Imamoglu, I.: Affinity of clinoptilolite-based zeolites towards removal of Cd from aqueous solutions. Sep. Sci. Technol.**43**, 1191–1207 (2008)
41. Ghasemi, Z., Sourinejad, I., Kazemian, H., Rohani, S.: Application of zeolites in aquaculture industry: a review. Rev. Aquac. **10**, 75–95 (2018)
42. Guan, H., Bestland, E., Zhu, C., Zhu, H., Albertsdottir, D., Hutson, J., Simmons, C.T., Ginic-Markovic, M., Tao, X., Ellis, A.V.: Variation in performance of surfactant loading and resulting nitrate removal among four selected natural zeolites. J. Hazard. Mater. **183**, 616–621 (2010)
43. Guaya, D., Valderrama, C., Farran, A., Armijos, C., Cortina, J.L.: Simultaneous phosphate and ammonium removal from aqueous solution by a hydrated aluminum oxide modified natural zeolite. Chem. Eng. J. **271**, 204–213 (2015)
44. Guaya, D., Valderrama, C., Farran, A., Armijos, C., Cortina, J.L.: Simultaneous phosphate and ammonium removal from aqueous solution by a hydrated aluminum oxide modified natural zeolite. Chem. Eng. J.**271**, 204–213 (2015)
45. Gupta, V., Sadegh, H., Yari, M., Shahryari, G.R., Maazinejad, B., Chahardori, M.: Removal of ammonium ions from wastewater a short review in development of efficient methods (2015)
46. Han, Y., Hu, Y.-J., Lian, J., Yang, S.-Z., Qi, Z.-N.: Phosphorus removal performance and mechanism of modified zeolite using alum sludge acidified extraction liquid. Huan jing ke xue= Huanjing kexue **40**, 3660–3667 (2019)
47. Han, Z., Dong, J., Shen, Z., Mou, R., Zhou, Y., Chen, X., Fu, X., Yang, C.: Nitrogen removal of anaerobically digested swine wastewater by pilot-scale tidal flow constructed wetland based on in-situ biological regeneration of zeolite. Chemosphere **217**, 364–373 (2019)
48. Harbottle, M.J., Mantle, M.D., Johns, M.L., Van Herwijnen, R., Al-Tabbaa, A., Hutchings, T.R., Moffat, A.J., Ouki, S.K.: Magnetic resonance imaging of the effect of zeolite on lithium uptake in poplar. Environ. Sci. Technol. **41**, 3444–3448 (2007)
49. Hartmann, M., Machoke, A.G., Schwieger, W.: Catalytic test reactions for the evaluation of hierarchical zeolites. Chem. Soc. Rev. **45**, 3313–3330 (2016)
50. Hoang, P.H., Yoon, K.-B., Kim, D.-P.: Synthesis of hierarchically porous zeolite A crystals with uniform particle size in a droplet microreactor. RSC Adv. **2**, 5323–5328 (2012)
51. Hokkanen, S., Bhatnagar, A., Sillanpää, M.: A review on modification methods to cellulose-based adsorbents to improve adsorption capacity. Water Res. **91**, 156–173 (2016)
52. Huang, H., Xiao, D., Pang, R., Han, C., Ding, L.: Simultaneous removal of nutrients from simulated swine wastewater by adsorption of modified zeolite combined with struvite crystallization. Chem. Eng. J. **256**, 431–438 (2014)
53. Inglezakis, V., Stylianou, M., Loizidou, M., Zorpas, A.: Experimental studies and modeling of clinoptilolite and vermiculite fixed beds for Mn^{2+}, Zn^{2+}, and Cr^{3+} removal. Desalin. Water Treat. **57**, 11610–11622 (2016)

54. Inglezakis, V.J., Zorpas, A.A.: Handbook of Natural Zeolites. Bentham Science Publishers (2012)
55. Jakkula, V., Wani, S.: Zeolites: potential soil amendments for improving nutrient and water use efficiency and agriculture productivity. Sci. Rev. Chem. Commun. **8**, 1–15 (2018)
56. Khazaei, M., Sillanpää, M.E., Yavari, Z., Savadkoohi, M., Ghadiri, K., Mahvi, A.H.: Adsorption of EDTA from aqueous solution using HDTMA-modified zeolite. Middle East J. Sci. Res.**23**, 2232–2245 (2015)
57. Kolaković, S., Stefanović, D., Lemić, J., Milićević, D., Tomović, S., Trajković, S., Milenković, S.: Forming a filter media from zeolite modified with SDBAC for wastewater treatment process. Chem. Ind. Chem. Eng. Q. **20**, 361–369 (2014)
58. Kragović, M., Daković, A., Sekulić, Ž, Trgo, M., Ugrina, M., Perić, J., Gatta, G.D.: Removal of lead from aqueous solutions by using the natural and Fe (III)-modified zeolite. Appl. Surf. Sci. **258**, 3667–3673 (2012)
59. Kurniawan, T.A., Chan, G.Y., Lo, W.-H., Babel, S.: Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. Sci. Total Environ. **366**, 409–426 (2006)
60. Laurino, C., Palmieri, B.: Zeolite: “the magic stone”; main nutritional, environmental, experimental and clinical fields of application. Nutr. Hosp. **32**, 573–581 (2015)
61. Leggo, P.J., Ledésert, B., Christie, G.: The role of clinoptilolite in organo-zeolitic-soil systems used for phytoremediation. Sci. Total Environ. **363**, 1–10 (2006)
62. Leyva-Ramos, R., Jacobo-Azuara, A., Diaz-Flores, P., Guerrero-Coronado, R., Mendoza-Barron, J., Berber-Mendoza, M.: Adsorption of chromium (VI) from an aqueous solution on a surfactant-modified zeolite. Colloids Surf., A **330**, 35–41 (2008)
63. Leyva-Ramos, R., Jacobo-Azuara, A., Diaz-Flores, P., Guerrero-Coronado, R., Mendoza-Barron, J., Berber-Mendoza, M.: Adsorption of chromium (VI) from an aqueous solution on a surfactant-modified zeolite. Colloids Surf. A: Phys. Chem. Eng. Asp. **330**, 35–41 (2008)
64. Li, C., Dong, Y., Wu, D., Peng, L., Kong, H.: Surfactant modified zeolite as adsorbent for removal of humic acid from water. Appl. Clay Sci. **52**, 353–357 (2011)
65. Li, C.J., Zhang, Y.J., Chen, H., He, P.Y.: High value-added utilization of silica fume to synthesize ZSM-35 zeolite membrane for Cd^{2+} removal. Mater. Lett. **260**, 126940 (2020)
66. Li, H., Shi, W.-Y., Shao, H.-B., Shao, M.-A.: The remediation of the lead-polluted garden soil by natural zeolite. J. Hazard. Mater. **169**, 1106–1111 (2009)
67. Li, W., Li, J., Zhang, Y., Cheng, X., Bian, W.: Adsorption mechanism of ammonium from aqueous solutions by NaCl modified zeolite. China Environ. Sci.**36**, 3567–3575 (2016)
68. Lin, H., Yang, S., Zhang, W.-T., Ma, Q.-J.: Characterization and denitriding effect of microwave modified zeolite ecomaterials. J. Northeast. Univ.**36**, 129 (2015)
69. Lin, H., Zheng, Q.-Q., Dong, Y.-B.: Effect of $LaCl_3$ on physicochemical properties of clinoptilolites and nitrogen and phosphate removal performance as well as sterilization. Chin. Rare Earths **36**, 1–8 (2015)
70. Lin, J., Zhan, Y., Zhu, Z., Xing, Y.J.: Adsorption of tannic acid from aqueous solution onto surfactant-modified zeolite. J. Hazard. Mater.**193**, 102–111 (2011)
71. Liu, S., Ding, Y., Li, P., Diao, K., Tan, X., Lei, F., Zhan, Y., Li, Q., Huang, B., Huang, Z.: Adsorption of the anionic dye Congo red from aqueous solution onto natural zeolites modified with N, N-dimethyl dehydroabietylamine oxide. Chem. Eng. J.**248**, 135–144 (2014)
72. Llanes-Monter, M.M., Olguín, M.T., Solache-Ríos, M.: Lead sorption by a Mexican, clinoptilolite-rich tuff. Environ. Sci. Pollut. Res. Int.**14**, 397–403 (2007)
73. Lofù, A., Mastrorilli, P., Dell’Anna, M.M., Mali, M., Sisto, R., Vignola, R.: Iron (II) modified natural zeolites for hexavalent chromium removal from contaminated water. Arch. Environ. Prot. **42**, 35–40 (2016)
74. Mahmoodi, N.M., Saffar-Dastgerdi, M.H.: Zeolite nanoparticle as a superior adsorbent with high capacity: synthesis, surface modification and pollutant adsorption ability from wastewater. Microchem. J. **145**, 74–83 (2019)
75. Mahvi, A.H., Vosoughi, M., Mohammadi, M.J., Asadi, A., Hashemzadeh, B., Zahedi, A., Pourfadakar, S.: Sodium dodecyl sulfate modified-zeolite as a promising adsorbent for the removal of natural organic matter from aqueous environments. Health Scope **5** (2016)

76. Malamis, S., Katsou, E.: A review on zinc and nickel adsorption on natural and modified zeolite, bentonite and vermiculite: examination of process parameters, kinetics and isotherms. J. Hazard. Mater. **252**, 428–461 (2013)
77. Malekian, R., Abedi-Koupai, J., Eslamian, S.S., Mousavi, S.F., Abbaspour, K.C., Afyuni, M.: Ion-exchange process for ammonium removal and release using natural Iranian zeolite. Appl. Clay Sci. **51**, 323–329 (2011)
78. Matijašević, S., Zildžović, S., Stojanović, J., Đošić, M., Nikolić, J., Stojanović, M., Labus, N.: Removal of uranium (VI) from aqueous solution by acid modified zeolites. Zastita Mater. **57**, 551–558 (2016)
79. Mihajlović, M.T., Lazarević, S.S., Janković-Častvan, I.M., Kovač, J., Jokić, B.M., Janaćković, D.T., Petrović, R.D.: Kinetics, thermodynamics, and structural investigations on the removal of Pb^{2+}, Cd^{2+}, and Zn^{2+} from multicomponent solutions onto natural and Fe (III)-modified zeolites. Clean Technol. Environ. Policy **17**, 407–419 (2015)
80. Misaelides, P.: Application of natural zeolites in environmental remediation: a short review. Microporous Mesoporous Mater. **144**, 15–18 (2011)
81. Misaelides, P., Zamboulis, D., Sarridis, P., Warchoł, J., Godelitsas, A.: Chromium (VI) uptake by polyhexamethylene-guanidine-modified natural zeolitic materials. Microporous Mesoporous Mater. **108**, 162–167 (2008)
82. Motsi, T., Rowson, N., Simmons, M.: Adsorption of heavy metals from acid mine drainage by natural zeolite. Int. J. Miner. Process. **92**, 42–48 (2009)
83. Mudasir, M., Karelius, K., Aprilita, N.H., Wahyuni, E.T.: Adsorption of mercury (II) on dithizone-immobilized natural zeolite. J. Environ. Chem. Eng. **4**, 1839–1849 (2016)
84. Neolaka, Y.A., Supriyanto, G., Kusuma, H.S.: Adsorption performance of Cr (VI)-imprinted poly (4-VP-co-MMA) supported on activated Indonesia (Ende-Flores) natural zeolite structure for Cr (VI) removal from aqueous solution. J. Environ. Chem. Eng. **6**, 3436–3443 (2018)
85. Nguyen, M.-V., Lee, B.-K.: Removal of dimethyl sulfide from aqueous solution using cost-effective modified chicken manure biochar produced from slow pyrolysis. Sustainability **7**, 15057–15072 (2015)
86. Nikashina, V., Kats, E., Serova, I., Gembitski, P.A.: Uranium sorption by organozeolites and ferromagnetic organozeolites from waste water of special laundry. In: Combined and Hybrid Adsorbents, pp. 85–92. Springer (2006)
87. Nomura, J., Shima, H.: Adsorption of hydrocarbons and formation of carbocations over zeolites studied by IR spectroscopy. J. Jpn. Petrol. Inst. **51**, 274–286 (2008)
88. Oliveira, C., Rubio, J.: New basis for adsorption of ionic pollutants onto modified zeolites. Miner. Eng. **20**, 552–558 (2007)
89. Oter, O., Akcay, H.: Use of natural clinoptilolite to improve water quality: sorption and selectivity studies of lead (II), copper (II), zinc (II), and nickel (II). Water Environ. Res. **79**, 329–335 (2007)
90. Pabalan, R.T.: Multicomponent cation exchange in natural zeolites–experiments and thermodynamic model. In: Joint Meeting of The Geological Society of America Soil Science Society of America, American Society of Agronomy, Crop Science Society of America, Gulf Coast Association of Geological Societies with the Gulf Coast Section of SEPM, Houston (2008)
91. Pérez-Ramírez, J., Christensen, C.H., Egeblad, K., Christensen, C.H., Groen, J.C.: Hierarchical zeolites: enhanced utilisation of microporous crystals in catalysis by advances in materials design. Chem. Soc. Rev. **37**, 2530–2542 (2008)
92. Pich, B., Warmada, I.W., Hendrayana, H., Yoneda, T.: Modified natural zeolite and bentonite as adsorbents of heavy metal ions from polluted groundwater in Yogyakarta urban area, Indonesia. J. Appl. Geol. **2** (2010)
93. Pitcher, S., Slade, R., Ward, N.: Heavy metal removal from motorway stormwater using zeolites. Sci. Total Environ. **334**, 161–166 (2004)
94. Polat, E., Karaca, M., Demir, H., Onus, A.N.: Use of natural zeolite (clinoptilolite) in agriculture. J. Fruit Ornam. Plant Res. **12**, 183–189 (2004)
95. Pratomo, S.W., Mahatmanti, F.W., Sulistyaningsih, T.: Pemanfaatan zeolit alam teraktivasi H_3PO_4 sebagai adsorben ion logam Cd (II) dalam larutan. Indones. J. Chem. Sci. **6**, 161–167 (2017)

96. Princz, P., Olah, J., Smith, S., Hatfield, K., Litrico, M.: Wastewater treatment using modified natural zeolites. In: Use of Humic Substances to Remediate Polluted Environments: From Theory to Practice, pp. 267–282. Springer (2005)
97. Puspitasari, T., Ilmi, M., Nurdini, N., Mukti, R.R., Radiman, C.L., Darwis, D., Kadja, G.T.M.: The physicochemical characteristics of natural zeolites governing the adsorption of Pb^{2+} from aqueous environment. Key Eng. Mater. **811**, 92–98 (2019)
98. Puspitasari, T., Kadja, G., Radiman, C., Darwis, D., Mukti, R.: Two-step preparation of amidoxime-functionalized natural zeolites hybrids for the removal of Pb^{2+} ions in aqueous environment. Mater. Chem. Phys. **216**, 197–205 (2018)
99. Qin, P., Xi, M., Li, J., Kong, F., Li, Y., Wang, J.: Effects of phosphorus removal by zeolite modified by ferric trichloride. Wetl. Sci.**15**, 464–469 (2017)
100. Qiu, M., Qian, C., Xu, J., Wu, J., Wang, G.: Studies on the adsorption of dyes into clinoptilolite. Desalination **243**, 286–292 (2009)
101. Ramesh, K., Reddy, D.D.: Zeolites and their potential uses in agriculture. Adv. Agron. **113**, 219–241 (2011)
102. Reeve, P.J., Fallowfield, H.J.: Natural and surfactant modified zeolites: a review of their applications for water remediation with a focus on surfactant desorption and toxicity towards microorganisms. J. Environ. Manage. **205**, 253–261 (2018)
103. Ren, H., Jiang, J., Wu, D., Gao, Z., Sun, Y., Luo, C.: Selective adsorption of Pb (II) and Cr (VI) by surfactant-modified and unmodified natural zeolites: a comparative study on kinetics, equilibrium, and mechanism. Water, Air, Soil Pollut. **227**, 101 (2016)
104. Renni, C.P., Mahatmanti, F.W., Widiarti, N.: Pemanfaatan Zeolit Alam Teraktivasi HNO_3 sebagai Ion Logam Fe (III) dan Cr (VI). Indones. J. Chem. Sci. **7**, 64–70 (2018)
105. Rhodes, C. J.: Properties and applications of zeolites. Sci. Progr., 223–284 (2010)
106. Sancho, I., Licon, E., Valderrama, C., de Arespacochaga, N., López-Palau, S., Cortina, J.: Recovery of ammonia from domestic wastewater effluents as liquid fertilizers by integration of natural zeolites and hollow fibre membrane contactors. Sci. Total Environ. **584**, 244–251 (2017)
107. Sannino, F., Ruocco, S., Marocco, A., Esposito, S., Pansini, M.: Cyclic process of simazine removal from waters by adsorption on zeolite HY and its regeneration by thermal treatment. J. Hazard. Mater. **229**, 354–360 (2012)
108. Schulze-Makuch, D., Bowman, R.S., Pillai, S.: Removal of biological pathogens using surfactant-modified zeolite. Google Patents (2007)
109. Seifi, L., Torabian, A., Kazemian, H., Bidhendi, G.N., Azimi, A.A., Charkhi, A.: Adsorption of petroleum monoaromatics from aqueous solutions using granulated surface modified natural nanozeolites: systematic study of equilibrium isotherms. Water Air Soil Pollut. **217**, 611–625 (2011)
110. Serati-Nouri, H., Jafari, A., Roshangar, L., Dadashpour, M., Pilehvar-Soltanahmadi, Y., Zarghami, N.: Biomedical applications of zeolite-based materials: a review. Mater. Sci. Eng., C **116**, 111225 (2020)
111. Shang, H.-J., Zhou, Y.-L., Zhao, Y., Zhao, D., Zhang, S.-H., Zhang, G., Zheng, X.-M.: Application progress of zeolite in removal of ammonia from wastewater. Mod. Chem. Ind. **33**, 26–29 (2013)
112. Shi, J., Yang, Z., Dai, H., Lu, X., Peng, L., Tan, X., Shi, L., Fahim, R.: Preparation and application of modified zeolites as adsorbents in wastewater treatment. Water Sci. Technol. **2017**, 621–635 (2018)
113. Shi, W.-Y., Shao, H.-B., Li, H., Shao, M.-A., Du, S.: Co-remediation of the lead-polluted garden soil by exogenous natural zeolite and humic acids. J. Hazard. Mater. **167**, 136–140 (2009).
114. Song, W., Shi, T., Yang, D., Ye, J., Zhou, Y., Feng, Y.: Pretreatment effects on the sorption of Cr (VI) onto surfactant-modified zeolite: mechanism analysis. J. Environ. Manage. **162**, 96–101 (2015)
115. Sprynskyy, M., Buszewski, B., Terzyk, A.P., Namieśnik, J.: Study of the selection mechanism of heavy metal (Pb^{2+}, Cu^{2+}, $Ni2^{+}$, and Cd^{2+}) adsorption on clinoptilolite. J. Colloid Interface Sci. **304**, 21–28 (2006)

116. Syafalni, S., Sing, S., Zawawi, M.: Sorption of dye wastewater by using natural zeolite, anionic-cationic surfactant modified zeolite and cationic surfactant modified zeolite. World Appl. Sci. J. **32**, 818–824 (2014)
117. Taffarel, S.R., Rubio, J.: Adsorption of sodium dodecyl benzene sulfonate from aqueous solution using a modified natural zeolite with CTAB. Miner. Eng.**23**, 771–779 (2010)
118. Tahervand, S., Jalali, M.: Sorption and desorption of potentially toxic metals (Cd, Cu, Ni and Zn) by soil amended with bentonite, calcite and zeolite as a function of pH. J. Geochem. Explor. **181**, 148–159 (2017)
119. Tang, Q., Chen, N.: Progress in research on natural zeolite modified methods. Mater. Rev. **23**, 439–441 (2009)
120. Tschegg, C., Rice, A.H.N., Grasemann, B., Matiasek, E., Kobulej, P., Dzivák, M., Berger, T.: Petrogenesis of a large-scale Miocene zeolite tuff in the eastern Slovak republic: the Nižný Hrabovec open-pit clinoptilolite mine. Econ. Geol. **114**, 1177–1194 (2019)
121. Vaclavikova, M., Stefusova, K., Ivaničová, L., Jakabsky, S., Gallios, G.: Magnetic zeolite as arsenic sorbent. In: Water Treatment Technologies for the Removal of High-Toxicity Pollutants, pp. 51–59. Springer (2009)
122. Valdés, M., Pérez-Cordoves, A.I., Marta Elena, D.G.: Zeolites and zeolite-based materials in analytical chemistry. TrAC, Trends Anal. Chem. **25**, 24–30 (2006)
123. Vintró, L.L., Smith, K.J., Lucey, J.A., Mitchell, P.I.: The environmental impact of the Sellafield discharges. In: Scope-Radsite Workshop, Brussels (2000)
124. Waghmare, S., Arfin, T., Rayalu, S., Lataye, D., Dubey, S., Tiwari, S.: Adsorption behavior of modified zeolite as novel adsorbents for fluoride removal from drinking water: surface phenomena, kinetics and thermodynamics studies. Int. J. Sci., Eng. Technol. Res.**4**, 4114–4124 (2015)
125. Wajima, T., Shimizu, T., Yamato, T., Ikegami, Y.: Removal of NaCl from seawater using natural zeolite. Toxicol. Environ. Chem. **92**, 21–26 (2010)
126. Walcarius, A.: Electroanalytical applications of microporous zeolites and mesoporous (organo) silicas: recent trends. Electroanal.: Int. J. Devoted Fundam. Pract. Asp. Electroanal. **20**, 711–738 (2008)
127. Wang, H., Xu, J., Sheng, L.: Purification mechanism of sewage from constructed wetlands with zeolite substrates: a review. J. Clean. Prod. **258**, 120760 (2020)
128. Wang, H., Zhang, H., Jiang, J.-Q., Ma, X.: Adsorption of bisphenol A onto cationic-modified zeolite. Desalin. Water Treat.**57**, 26299–26306 (2016)
129. Wang, L., Zhang, Z., Ding, A., Cheng, R., Zhang, M., Wu, D.: Modification of zeolite materials and their adsorption properties for the pollutants in aqueous solution. Chem. Ind. Eng. Prog. **37**, 2269–2281 (2018)
130. Wang, Q., Yang, Z., Wang, L.: Study on ammonia nitrogen sorption by the modified zeolite. Technol. Water Treat. **12**, 77–81 (2015)
131. Wang, Q., Yang, Z., Wang, L.: Study on ammonia nitrogen sorption by the modified zeolite. Technol. Water Treat.**12**, 77–81 (2015)
132. Wang, S., Peng, Y.: Natural zeolites as effective adsorbents in water and wastewater treatment. Chem. Eng. J. **156**, 11–24 (2010)
133. Widiastuti, N., Wu, H., Ang, H.M., Zhang, D.: Removal of ammonium from greywater using natural zeolite. Desalination **277**, 15–23 (2011)
134. Widiastuti, N., Wu, H., Ang, M., Zhang, D.-K.: The potential application of natural zeolite for greywater treatment. Desalination **218**, 271–280 (2008)
135. Wingenfelder, U., Furrer, G., Schulin, R.: Sorption of antimonate by HDTMA-modified zeolite. Microporous Mesoporous Mater. **95**, 265–271 (2006)
136. Yang, B., Lin, H., Dong, Y.: Effects of NaOH pretreatment and NaCl/roasting modification on properties of ammonia-nitrogen removal of zeolite. J. Chin. Ceram. Eng. **2**, 303–311 (2017)
137. Yang, M., Lin, J., Zhan, Y., Zhang, H.: Adsorption of phosphate from water on lake sediments amended with zirconium-modified zeolites in batch mode. Ecol. Eng.**71**, 223–233 (2014)
138. Zanin, E., Scapinello, J., de Oliveira, M., Rambo, C.L., Franscescon, F., Freitas, L., de Mello, J.M.M., Fiori, M.A., Oliveira, J.V., Dal Magro, J.: Adsorption of heavy metals from wastewater

graphic industry using clinoptilolite zeolite as adsorbent. Process Saf. Environ. Prot. **105**, 194–200 (2017)

139. Zhang, X., Gao, J., Zhao, S., Lei, Y., Yuan, Y., He, C., Gao, C., Deng, L.: Hexavalent chromium removal from aqueous solution by adsorption on modified zeolites coated with Mg-layered double hydroxides. Environ. Sci. Pollut. Res.**26**, 32928–32941 (2019)
140. Zhang, Y., Dong, J., Guo, F., Shao, Z., Wu, J.: Zeolite synthesized from coal fly ash produced by a gasification process for Ni^{2+} removal from water. Minerals **8**, 116 (2018)
141. Zhao, H., Vance, G.F., Urynowicz, M.A., Gregory, R.W.: Integrated treatment process using a natural Wyoming clinoptilolite for remediating produced waters from coalbed natural gas operations. Appl. Clay Sci. **42**, 379–385 (2009)
142. Zhu, B., Chen, X., Yang, W., Ji, H.: Characterization of trace mercury adsorption by modified zeolite. Chinese J. Environ. Eng. **10** (2016)
143. Zieliński, M., Zielińska, M., Dębowski, M.: Ammonium removal on zeolite modified by ultrasound. Desalin. Water Treat. **57**, 8748–8753 (2016)
144. Zieliński, M., Zielińska, M., Dębowski, M.: Ammonium removal on zeolite modified by ultrasound. Desalin. Water Treat.**57**, 8748–8753 (2016)
145. Zuo, S., Jing, Z., Tao, M.: Study on the application of natural zeolite and modified zeolite in wastewater treatment. Appl. Chem. **48**, 1136–1145 (2019)

Application of Clay Composites for Microplastics Removal from Environment

Munir Ahmad, Hina Rasheed, Jahangir Ahmad, Nahrir M. A. Lubis, Muhammad Imran Rafique, Mutair A. Akanji, Mohammad I. Al-Wabel, and Abdullah S. F. Al-Farraj

Abstract Extensive utilization of plastic has resulted in elevated levels of microplastics (MPs) in environment, which requires immediate attention. Mismanagement, degradation of plastic waste, MPs-laden dust particles, industrial and agricultural activities, as well as plastic bottles and utensils are responsible for MPs pollution in environment. Clay, which is characterized by smaller particle size, higher stability, lamellar structure, high surface area, and high ion exchange capacity, can be used for MPs removal from contaminated media via coagulation-flocculation, degradation, and adsorption. Therefore, the prevalence of MPs in environment, influences of MPs toxicity on human, as well as removal technique have been discussed in this chapter. Application of clay-based materials in removing MPs is a promising technique; however, natural clays are inefficient for anionic MPs removal due to electrostatic repulsion. Thus, modification of clays with foreign materials could be a cheaper, efficient, and environment-friendly technology for complete removal of MPs; nevertheless, very limited studies have been conducted on this subject so far. Therefore, cheaper and efficient clay-based composites should be fabricated to remove/degrade MPs from environment. Further, the existence of MPs in the environment, transport of MPs between various environmental compartments, and interactions of MPs with co-existing materials should be explored in the future.

Keywords Emerging pollutants · Adsorption · Degradation · Stabilization · Water treatment

---

M. Ahmad (✉) · J. Ahmad · N. M. A. Lubis · M. I. Rafique · M. A. Akanji · M. I. Al-Wabel · A. S. F. Al-Farraj
Soil Sciences Department, College of Food and Agricultural Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia
e-mail: amunir@ksu.edu.sa

H. Rasheed
Department of Soil Science, Faculty of Agriculture and Environment, The Islamia University of Bahawalpur, Bahawalpur 63100, Pakistan

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_18

1 Introduction

Plastic, which is basically a combination of various synthetic polymer constituents, has gained immense importance as a so-called essential material due to its economical, stable, lightweight, and versatile properties. It has various applications in agricultural, pharmaceuticals, industrial product packing and transport, and a number of household activities. Consequently, global demand and output of plastic-based products are increasing annually. Worldwide production of polyethylene and polypropylene showed an annual increase of 7% [1]. Extensive utilization of plastic products has instigated microplastics (MPs) pollution worldwide in recent times. The global plastics production crossed 4.90 billion tons in 2015, which could reach up to 12.0 billion tons by 2050 [2]. About 19–23 million tons of plastic waste was released into marine environments in 2016, which is expected to reach up to 53 million tons per annum by 2030 [3]. The accumulated plastics are degraded by various atmospheric agents including solar radiations, waves, abrasion, ultraviolet radiations, photo-oxidation, microbial activities, and mechanical forces, which consequently generates MPs (less than 5 mm size) and nano-plastics (1.0–100 nm size) fragments [4, 5]. These degraded plastic products are termed as secondary MPs. Moreover, micro- and nano-sized plastics are also produced, which directly enter into the ecosystem, and are referred as primary MPs [6]. Constant dumping of plastic-based waste in environment including soil and water resources has resulted in the accumulation of polymer debris in soil and aquatic phase causing severe environmental pollution. This plastic debris gradually accumulates as MPs in diverse ecological components including drinking water and food, eventually in the human body [7, 4]. Once these MPs accumulate in the terrestrial and aquatic environments, they integrate with soil nutrients making them potentially unavailable for plants, incorporate in foodstuff including seafood, salts, and drinking water, and ultimately become a potential threat for terrestrial and marine life [8–10]. Therefore, ubiquitous release of MPs by mismanagement of plastic waste resulted in long-lasting toxicity and intensive environmental pollution.

According to an estimate, the plastic waste release into the environment could reach up to 12 billion tons by the year 2050, which is 60% higher than the current plastic waste dumping value [2]. This amount of plastics in the environment may result in the accumulation of large volumes of MPs in human beings. This situation is even worst in the Kingdom of Saudi Arabia (KSA), as it consumes 20-folds more plastic products as compared to the global average, consequently releasing large volumes of MPs into the environment. Hence, the mishandling of plastic waste and accumulation of MPs in the environment pose a threat to environmental sustainability. Despite the great danger that MPs pollution poses, little research has been done on their potential health risks to humans. Thus, sources and prevalence of MPs in food and drink items must be explored to avoid hazardous effects on the ecosystem. In addition, new cost-effective and environmentally friendly technologies are needed to reduce the presence and release of MPs into the environment. Therefore, the presence of MPs in the environment and their effects on human health will be reviewed and discussed in this chapter. Moreover, the effectiveness of clay-based materials in removing, degrading, and stabilizing MPs in contaminated media will be discussed in details.

2 Microplastics: A Potential Environmental Threat

2.1 Occurrence of MPs in the Environment

The MPs can be found in various environmental compartments such as air, bottled water, groundwater, freshwater, tap water, aquatic environments, and dietary products. Usually, indoor environments have higher amounts of MPs (1–60 fibers m^{-3}) than outdoor environments (0.3–1.5 fibers m^{-3}) [11]. Vianello et al. [12] reported that 59%–92% polyester, 5%–28% polyethylene, 0.4%–10% polypropylene, and 0%–13% nylon were present in the air samples collected from an apartment. Likewise, Zhang et al. [13] found that 33%–47% of polyester-based MPs were present in samples collected from the indoor environment in China. These MPs in the air get deposited onto various household utensils, drinks, and food items, consequently ending up in humans. Cai et al. [14] reported that the deposition rate of MPs varies from 175 to 313 particles m^{-2} day^{-1}. Brahney et al. [15] and Allen et al. [16] reported that the mean deposition rate of MPs was 132 and 365 particles m^{-2} day^{-1}, respectively.

The occurrence of MPs has been reported in water resources globally as well. Di and Wang [17] reported that 1597 to 12,611 particles m^{-3} were present in surface water samples collected from China. In another study, Jiang et al. [18] found 617 and 2316 particles m^{-3} in surface water samples of China. Generally, the amount of MPs varies from 0 to 5.4×10^7 particles L^{-1} in drinking water [19]. However, Uhl et al. [20] reported that MPs could be present up to 6.3×10^3 particles L^{-1} in glass water bottles. The amount of MPs in bottled water varies from 0 to 5.4×10^7 particles L^{-1} [21]. Mason et al. [22] conducted a study and concluded that 93% of drinking bottled water contains MPs (10.4 particles of MPs L^{-1}). Likewise, Oßmann et al. [10] conducted a study and reported the presence of MPs in 32 different bottled water in the range of 2649–6292 particles L^{-1}. Average concentrations of MPs in water samples have also been presented in Table 1.

Several studies reported the frequent detection of MPs in foodstuff too. It has been estimated that human beings can ingest from 37 to a billion MPs particles via foodstuff per annum [24]. It has been reported that sea salt contained 550–681 particles kg^{-1} of MPs, while honey and sugars, and beer contained 32 and 12–109 particles kg^{-1}, respectively [25] . In a study, Du et al. [26] found that 3–29 particles of MPs $container^{-1}$ were detected in take-out meal plastic containers. The occurrence of MPs in fish was reported in the range of 0–48 particles $individual^{-1}$ [27]. The number of MPs in shellfish was detected to be 0–57.2 particles g^{-1}, which is higher than the number of MPs in fish [28]. Besides, MPs have been found in more than 100 brands of table salt globally. Table salt samples collected from Croatia contained up

Table 1 Average concentration of microplastics in water samples. *Source* [23]

Water type	Sample processing	Identification	Average concentration (MPs m^{-3})
Bottled water	Vacuum filtration	Micro-Raman spectroscopy	1.40×10^4
Bottled water	Nile red solution	Optical microscope and FTIR	3.25×10^5
Bottled water	EDTA solution	Micro-Raman spectroscopy	2.65×10^6
Tap water	Rose bengal	Optical microscope	4.00×10^{-1}
DWTPs	Digestion with wet peroxide	FTIR and Raman spectroscopy	4.69×10^5

Note FTIR: Fourier transform infrared spectroscopy, EDTA: ethylene diamine tetraacetic acid tetra sodium, and DWTPs: drinking water treatment plants

to 1.98×10^4 particles per kg [29]. Another study demonstrated the occurrence of 7 particles oyster^{-1}, 15 particles fish^{-1}, and 3.7 particles mussel^{-1} [30]. Additionally, it has been seen that the number of MPs are more in fruits as compared to vegetables [31]. Golwala et al. [30] stated that around 300,000 particles kg^{-1} of MPs were detected in food waste collected from a grocery store. Therefore, it is an urgent need of time to limit the use of plastics in drink and food items, during the preparation and packaging process, so that the hazardous impacts of MPs could be avoided. Moreover, the occurrence of MPs has been reported in commercial dietary and drink products worldwide including canned fish, mineral water, salt, sugar, honey, and beverages. For instance, 0.36–0.47 particles g^{-1} of MPs were found in two species of commercially grown bivalves [32]. Likewise, 0.15 particle g^{-1} of MP was reported in four commercial bivalves in South Korea [33]. Hernandez et al. [34] reported that around 11.6 billion MPs can be released into a single cup of tea from teabag brewed at 95°C. Similarly, 118–6292 MPs L^{-1} of bottled water is reported [35]. Fadare et al. [24] reported the presence of 3.0–38 mg of MPs per pack of plastic-based disposable utensils. They concluded that new plastic containers can potently release more MPs into food and beverages subsequently deteriorating the human health. Alike, Du et al. [26] suggested that people consuming take-out food 4–7 times in a week are at risk to ingest 12–203 particles of MPs into their body. Mason et al. [22] found that 93% of drinking bottled water contained traces of MPs, with an average of 10.4 particles of MPs L^{-1}. Similarly, Oßmann et al. [10] analyzed MPs in 32 different mineral water bottles and detected MPs in all of them. They stated that the number of MPs in those bottled water was in the range of 2649–6292 particles L^{-1}.

Elevated concentrations of MPs have been frequently detected in aquatic environments, drinking water, lakes, soil, food items, and even in the body of human beings. Landfilling, pharmaceutical vectors, makeups, nail polish, shower gels, toothpaste, personal care products, glitter, 3D printers, face cleanser, hair coloring, drilling fluids, sunscreen, synthetic textiles, and industrial abrasives are among the major sources of MPs [36, 37]. The involvement of various industries in the generation of MPs is shown in Fig. 1. MPs could be made of poly (N-methyl acrylamide), polyvinyl chloride rayon, polyethylene, alkyd resin, polyester, polyethylene terephthalate, epoxy resin, polyacrylonitrile, ethylene–vinyl acetate, nylon, acrylic, polyamide, and many more and may occur in the environment as foams, fragments, shafts, films, granules, and fibers [30, 36]. Thus, consumption of seafood, food items packed in plastic containers, plastic teabags, take-out food containers, disposable plastic utensils, and bottled water could result in the accumulation of MPs in the body of human beings.

The quantity of MPs in various materials vary extensively based on the size of MPs and the surrounding environment. For example, Mintenig et al. [38] reported the presence of only 7 MP m^{-3} (lower detection limit 20 μm), while in contrast, Schymanski et al. [39] and Oßmann et al. [10] reported that an enormous amount of MPs is present in bottled water of different bottled mineral waters. The number of MPs also varied with packaging materials such as Schymanski et al. [39] observed 88–118 MP L^{-1} in reused polyethylene terephthalate bottles and 50 MP L^{-1} in reused glass bottles; however, in one time used polyethylene terephthalate bottles, 14 MP L^{-1} were recorded by Oßmann et al. [10]. Furthermore, in addition to cleaning of bottles for reuse, carbonization and bottle age also play a significant role in the accumulation of MPs in water bottles [10]. On the other hand, there are enough chances of MPs accumulation in bottled water during cleaning of returnable bottles by certain chemicals to remove germs, odor and dirt particles, pumping of groundwater in bottles, and lastly application of synthetic-semisynthetic glue to paste paper or

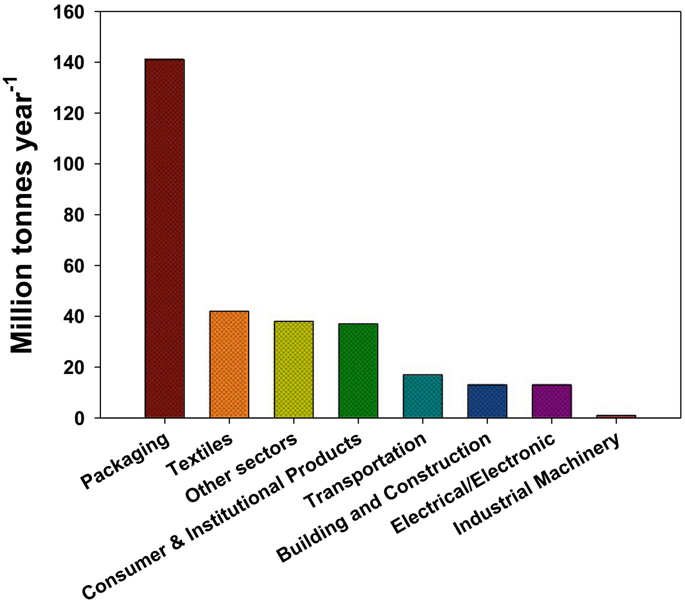


Fig. 1 Contribution of different industrial sectors in the generation of plastic waste globally. *Source* [2]

plastic labels on bottles [40]. Weisser et al. [41] stated a drastic increase in MPs in plastic capped bottles, which suggested plastic capping as one of the entry routes of MPs.

2.2 Impacts of MPs on Human Health

Various research studies have reported the occurrence of MPs in a variety of foodstuffs such as processed food, seafood, and drinking water including both bottled as well as tap water [41–43]. Until now aquatic environment-based food (seafood) was considered as the main pathway of MPs entry in the food chain; however, recent research studies found that consumption of processed food, canned food, ready to eat meals, and even tea bags are responsible for MP contamination [44–46]. For example, recently, Li et al. [47] found that feeding formula milk in plastic bottles might end up in ingestion of one million MPs in infants on daily basis. Similarly, studies have found that children and adults are exposed from dozens to 100,000 MPs per day from various sources, including air, drinking water, and consumption of seafood and processed foods [48].

Human beings are exposed to MPs toxicity via inhalation of MP-laden dust, ingestion of MPs containing food, and touching the MP debris [49]. Ingestion of MPs into the human body through food is considered as the major source of its accumulation in humans. According to an estimate, 39,000 to 52,000 MPs particles per person are consumed by human beings every year via food [50]. It has been reported that different food items including fish, mussels, salt, sugar, fruits, vegetables, shrimps, oysters, bottled beverages, canned food, honey, beer, and bivalves contain MPs [51]. For instance, 11,000 MP particles per person annually are being ingested into the human body in Europe via bivalves, and 37–100 MPs via salt in Europe and China [51]. The presence of about 550–681 and 32 MPs particles kg^{-1} in sea salt and honey/sugar, respectively, is reported, whereas, 12–109 and 28–241 MP particles L^{-1} in beer and returnable plastic bottles, respectively, are detected [25]. Furthermore, MPs may also entrap into the food items from external sources during food processing, storing, and transportation. For instance, settling of dust in plates and utensils and as well as utilization of disposable cups and plates may also contribute to MPs introduction to human body. Besides, nano- and micro-sized plastic particles leach from packaging material used for ready to eat food and accumulate in it [52]. According to an estimate, around 4000 particles of MPs are being ingested by humans via drinking water, 11,000 via shellfish, and 1000 via sea salt annually [53, 54]. Additionally, around 272 particles of MPs can be inhaled by human beings in a single day due to the occurrence of MPs in the air [12]. The MPs accumulation in the human body may result in respiratory dysfunction, neurotoxicity, reduction in lipid digestion, inhibition of digestive activities, consequently affecting the immune system and cell health. Therefore, contamination of food and drink items could be either through the accumulation of MPs inside the items or via external sources.

Exposure to MPs can potentially pose health risks to human beings. Recent reports demonstrated the presence of MPs in the human intestine, tissues, and placenta [55]. Generally, MPs are a mixture of various contaminates as they can effectively absorb heavy metals, pesticides, pharmaceuticals, pathogens, and persistent organic compounds [56]. Therefore, MPs are not only an ecological threat themselves, but also act as a vector for other environmentally hazardous pollutants, which eventually leads to various abnormalities in human beings such as diabetes, cancer, obesity, endocrine disturbance, reproductive impairments, and cardiovascular issues [56]. Accumulation of MPs may lead to the damage of DNA, disruption of the digestive system, respiratory diseases [57]. Additionally, exposure to MPs may lead to asthma, bone impaction, respiratory bronchiolitis, and gastrointestinal dysfunction in human beings [58]. Fewer studies have reported the mutagenic, carcinogenic, and hazardous environmental impacts on MPs [59–61]. Therefore, the magnitude of the problem due to MPs pollution is getting bigger with each passing day, which needs immediate attention to be resolved for sustainable human health and ecosystem (Fig. 2).

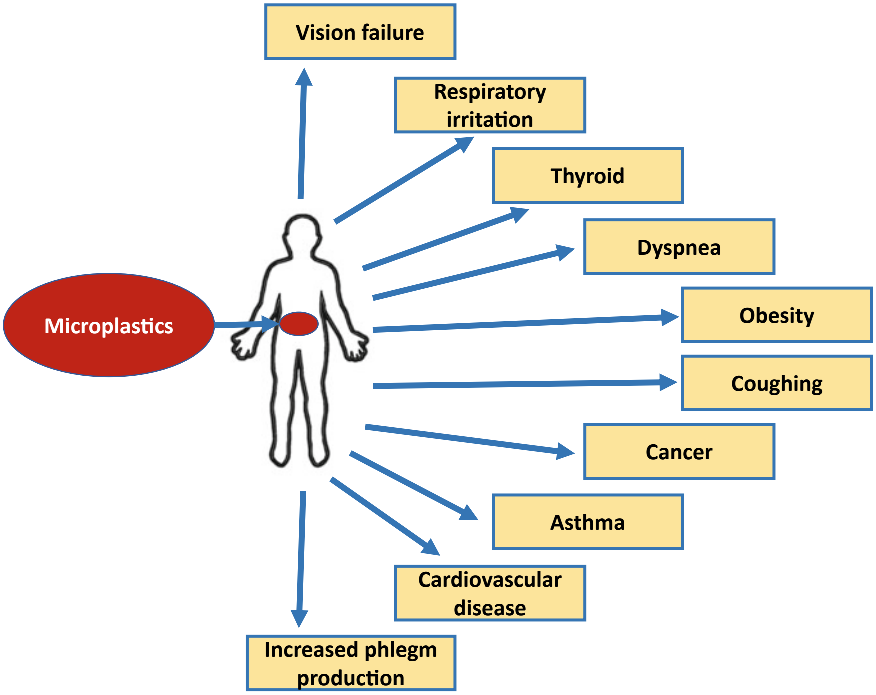


Fig. 2 Potential health impacts of plastics on human. *Source* [62, 63]

3 MPs Removal Technologies

Numerous miscellaneous approaches including activated sludge, membrane bioreactor, magnetic carbon nanotube, ultrafiltration, adsorption, electrodialysis, coagulation, and membrane separation have been used by various researcher to remove hazardous pollutants from the environment [64]. However, majority of these techniques are either expensive or inefficient in completely removing the pollutants from the contaminated media. Therefore, adsorption is the most commonly accepted technique due to lower cost, simplicity, easy operation, and high efficiency [65, 66]. Nevertheless, the selection of an appropriate and efficient adsorbent is of significant importance. A range of natural and synthetic adsorbents such as biochar, clay, metal hydroxides, activated carbon, and carbon nanotubes have been developed and employed by various researchers to treat contaminated media, but a very little is known about their performance for MPs removal. Therefore, researchers around the world are in continuous search of developing low-cost, environment-friendly, and highly efficient adsorbents to remove various environmental pollutants such as MPs.

4 MPs Removal Through Clay-Based Materials

Natural clays are abundantly found around the globe and are thus cheaper and accessible. Therefore, clays have been widely employed in various fields from ceramics to industries and environment. Due to layered structure, higher cation exchange capacity and surface area, clays can potentially remove environmental pollutants. Moreover, various researchers have modified the natural clays with different physical, chemical, mechanical, and biological approaches to further improve their properties for targeted applications [67].

Due to the presence of exchangeable cations and anions on the surface of clays, these can effectively be used for water purification [68]. Therefore, owing to unique characteristics such as cheaper, abundance, and high surface area, natural and modified clays can solve the environmental pollution problem. Beside other potent environmental pollutants, clays can also be used for the removal of MPs from various environmental matrices. Natural clays and colloids are found globally and can potentially interact with plastic particles, subsequently hindering their transport/mobility in the environment [53, 54]. For instance, Li et al. [69] conducted a study to understand the interaction of both negatively and positively charged MPs with kaolinite clay, and found that kaolinite clay particles could effectively adsorb MPs particles on their surfaces by generating plastic-kaolinite heteroaggregates, consequently affecting the transport of MPs in porous media. It was concluded that the surface charge is one of the critical factors in predicting the movement and retention of MPs in the environment [69]. In another study, Shen et al. [70] reported that porous and rough surface of clay-based materials can effectively remove plastic microspheres. Some of the reports suggested that MPs particles can aggregate with suspended clay

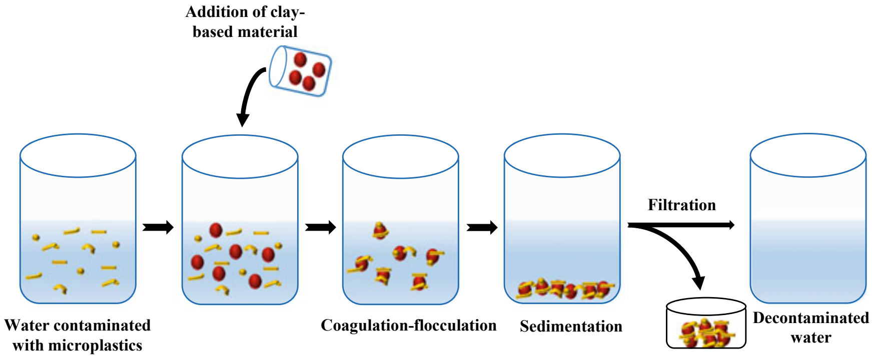


Fig. 3 Schematic representation of the coagulation-flocculation and sedimentation process to separate microplastics particles from contaminated water using clay-based materials

particles, subsequently resulting in the sedimentation, which is one of the important mechanisms to decontaminated MPs-laden water [71]. Likewise, Wagner and Lambert [72] suggested that the generation of heteroaggregates of MPs with natural clay particles in water is an important factor for rapid sedimentation resulting in reduced transport/mobility of MPs. Pivokonský et al. [73] reported that coagulation-flocculation coupled with sedimentation using clay resulted in efficient removal of MPs from water. Furthermore, it was stated that the removal efficiency was independent of the shape and size of MPs [73]. While, some reports suggest that size along with other characteristics including shape, surface charge, chemical composition, and reactivities of MPs affect the removal process [74–76]. Moreover, pH and ionic strength, as well as presence of proteins, other ions, natural organic matter, and colloids affect the removal and transformation of MPs from water [75]. Figure 3 shows a schematic representation of the coagulation-flocculation and sedimentation process to separate MPs from contaminated water using clay-based materials. In addition to the coagulation-flocculation and sorption processes, the porous structure of clay minerals may result in multilayer sorption of MPs onto their surfaces [75].

Clay minerals may degrade and transform the MPs, subsequently reducing their contents in the environment [77]. Recently, Ding et al. [78] explored the degradation of polyvinyl chloride and poly(ethylene terephthalate) by using kaolinite and montmorillonite clay minerals. It was revealed that the clay minerals enhanced the degradation and aging process of aforementioned MPs through generating •OH species.

It has been reported that MPs could be degraded via microbial, thermal, and photodegradation processes; while, photolysis has been considered to play the major role in non-biological aging of MPs in the environment [53, 54]. Reactive oxygen species such as •OH, singlet oxygen, and superoxide anion radical are formed with UV radiations subsequently generating O-containing functional groups on MPs, which further results in the degradation of the polymers [79]. Furthermore, the addition of clay minerals may further increase the photodegradation/phototransformation of the MPs in the environment due to the occurrence of Lewis base-catalyzed alkalization on the surface of clay minerals [80]. Despite of few studies about MPs degradation through clay minerals, the complete mechanisms of degradation and overall fate are not completely understood and need further in-depth explorations.

5 Removal of MPs by Using Clay-Based Composites

Despite of the widespread application of clay-based adsorbents to remove various pollutants from the environment, natural clays are inefficient in removing anionic pollutants from the environment completely. The net negative surface charge of natural clay minerals may develop electrostatic repulsive forces with the anionic contaminants, subsequently resulting in poor performance for the removal of such contaminants from the polluted media. In this scenario, some researchers have modified the natural clays with foreign materials to fabricate clay-based composites and observed improved anionic retention capacity of such composite materials [81]. MPs are considered to have either positive or negative surface charges and thus can effectively be removed through charged adsorbents. However, the interactions of MPs with charged species have not yet been explored completely [82]. Therefore, the modification of natural clays by adding foreign materials could alter the surface charge of the resultant composite and may improve its adsorption efficiency for particular MPs. For instance, Zhang et al. [83] stated that bonding of polystyrene nano-plastic particles with clay minerals such as kaolinite and montmorillonite was very weak due to net negatively charged surfaces, which might have developed electrostatic repulsive forces. Similarly, another study concluded that bentonite clay has lower adsorption of polystyrene-based MPs due to the development of repulsive forces [84].

Modification of natural clays with foreign materials could be an effective method to enhance sorption capacity of clay-based materials for MPs removal. Recently, Huang et al. [85] investigated the efficiency of clay-based composite materials for MPs removal from water. It was revealed that the modification of kaolin with Fe exhibited a removal capacity of 13.68 mg g^{-1} towards MPs, whereas modification with Co/Mn increased the adsorption capacity of kaolin up to 22 mg g^{-1}. Similarly, Shen et al. [70] modified the aluminosilicate clay minerals by using cationic surfactants to remove MPs from the environment. It was observed that such modification could remove more than 96% of polyethylene and polyamide MPs. In another study, Singh et al. [86] reported that the addition of NaCl could decrease the electrostatic repulsion between clay and MPs, hence, improving its removal. Additionally, the presence of Na^+ ions may improve the aggregation process through bridging the negatively charged species, i.e., clay and MPs. Therefore, modifying the clay minerals with foreign materials and compositing them with other carrier materials could result in enhanced removal/degradation of MPs from the environment; however, limited studies have been conducted so far to understand the efficiency of various clay-based composites for MPs removal.

6 Conclusion

Despite the increasing concerns about the occurrence of MPs in the environment, the studies about MPs fate, removal, degradation, and sorption process are limited. Owing to unique properties, low-cost, abundance, and high surface area, use of clay-based materials could be an efficient and environment-friendly technique to remove MPs from the environment. Coagulation-flocculation followed by sedimentation are the most common mechanisms for immobilization/removal of MPs from water sources using clay-based materials. Moreover, the presence of clay minerals has been seen to boost degradation and photolysis process; nevertheless, very little have been explored in this context. Natural inorganic clay minerals are inefficient in removing anionic pollutants from the environment completely due to the generation of electrostatic repulsive forces between anionic contaminants and clay. Thus, researchers have modified/activated the natural clays with foreign materials to fabricate clay-based composites to improve MPs retention capacity of such composite materials. However, limited studies have been conducted so for to understand the effectiveness of different clay-based composite materials for MPs removal/degradation. Therefore, developing low-cost, environment-friendly, and highly efficient adsorbents to remove various environmental MPs still remains a challenge for the researchers. There is dire need of time to develop efficient and cheaper composites with clay minerals for complete removal of MPs from environment. Further, the transport of MPs between various environmental compartments should be explored. Thus, future research should focus on exploring the occurrence of MPs in environment, their fate, transport, and interactions with co-occurring substances, and subsequent development of cheaper and efficient clay composites for complete removal of MPs from environment.

Acknowledgements The authors extend their appreciation to the Deputyship for Research & Innovation, "Ministry of Education" in Saudi Arabia for funding this research work through the project number (IFKSUDR_F161).

References

1. Andrady, A.L.: The plastic in microplastics: a review. Mar. Pollut. Bull. **119**, 12–22 (2017)
2. Geyer, R., Jambeck, J.R., Law, K.L.: Production, use, and fate of all plastics ever made. Sci. Adv. **3**, e1700782 (2017)
3. Walker, T.R.: (Micro) plastics and the UN sustainable development goals. Curr. Opin. Environ. Sci. Health 100497 (2021)
4. Ragusa, A., Svelato, A., Santacroce, C., Catalano, P., Notarstefano, V., Carnevali, O., Papa, F., Rongioletti, M.C.A., Baiocco, F., Draghi, S., D'Amore, E.: Plasticenta: first evidence of microplastics in human placenta. Environ. Int. **146**, 106274 (2021)
5. Silva, A.B., Bastos, A.S., Justino, C.I., da Costa, J.P., Duarte, A.C., Rocha-Santos, T.A.: Microplastics in the environment: challenges in analytical chemistry—a review. Anal. Chim. Acta **1017**, 1–19 (2018)

6. da Costa, J.P., Duarte, A.C., Rocha-Santos, T.A.: Microplastics—occurrence, fate and behaviour in the environment. In: Comprehensive Analytical Chemistry, vol. 75, pp. 1–24. Elsevier (2017)
7. Curren, E., Leaw, C.P., Lim, P.T., Leong, S.C.Y.: Evidence of marine microplastics in commercially harvested seafood. Front. Bioeng. Biotechnol. **8**, 1390 (2020)
8. Guo, J.J., Huang, X.P., Xiang, L., Wang, Y.Z., Li, Y.W., Li, H., Cai, Q.Y., Mo, C.H., Wong, M.H.: Source, migration and toxicology of microplastics in soil. Environ. Int. **137**, 105263 (2020)
9. Kumar, B.V., Löschel, L.A., Imhof, H.K., Löder, M.G., Laforsch, C.: Analysis of microplastics of a broad size range in commercially important mussels by combining FTIR and Raman spectroscopy approaches. Environ. Pollut. **269**, 116147 (2021)
10. Oßmann, B.E., Sarau, G., Holtmannspötter, H., Pischetsrieder, M., Christiansen, S.H., Dicke, W.: Small-sized microplastics and pigmented particles in bottled mineral water. Water Res. **141**, 307–316 (2018)
11. Dris, R., Gasperi, J., Mirande, C., Mandin, C., Guerrouache, M., Langlois, V., Tassin, B.: A first overview of textile fibers, including microplastics, in indoor and outdoor environments. Environ. Pollut. **221**, 453–458 (2017)
12. Vianello, A., Jensen, R.L., Liu, L., Vollertsen, J.: Simulating human exposure to indoor airborne microplastics using a Breathing Thermal Manikin. Sci. Rep. **9**, 1–11 (2019)
13. Zhang, Q., Zhao, Y., Du, F., Cai, H., Wang, G., Shi, H.: Microplastic fallout in different indoor environments. Environ. Sci. Technol. **54**, 6530–6539 (2020)
14. Cai, L., Wang, J., Peng, J., Tan, Z., Zhan, Z., Tan, X., Chen, Q.: Characteristic of microplastics in the atmospheric fallout from Dongguan city, China: preliminary research and first evidence. Environ. Sci. Pollut. Res. **24**, 24928–24935 (2017)
15. Brahney, J., Hallerud, M., Heim, E., Hahnenberger, M., Sukumaran, S.: Plastic rain in protected areas of the United States. Science **368**, 1257–1260 (2020)
16. Allen, S., Allen, D., Phoenix, V.R., Le Roux, G., Jiménez, P.D., Simonneau, A., Binet, S., Galop, D.: Atmospheric transport and deposition of microplastics in a remote mountain catchment. Nat. Geosci. **12**(5), 339–344 (2019)
17. Di, M., Wang, J.: Microplastics in surface waters and sediments of the Three Gorges Reservoir, China. Sci. Total Environ. **616**, 1620–1627 (2018)
18. Jiang, C., Yin, L., Wen, X., Du, C., Wu, L., Long, Y., Liu, Y., Ma, Y., Yin, Q., Zhou, Z., Pan, H.: Microplastics in sediment and surface water of west dongting lake and south dongting lake: abundance, source and composition. Int. J. Environ. Res. Public Health **15**, 2164 (2018)
19. Zhang, Q., Xu, E.G., Li, J., Chen, Q., Ma, L., Zeng, E.Y., Shi, H.: A review of microplastics in table salt, drinking water, and air: direct human exposure. Environ. Sci. Technol. **54**, 3740–3751 (2020)
20. Uhl, W., Eftekhardadkhah, M., Svendsen, C.: Mapping microplastic in Norwegian drinking water. Atlantic **185**, 491–497 (2018)
21. He, D., Luo, Y. (eds.): Microplastics in Terrestrial Environments: Emerging Contaminants and Major Challenges, vol. 95. Springer Nature (2020)
22. Mason, S.A., Welch, V.G., Neratko, J.: Synthetic polymer contamination in bottled water. Front. Chem. **6**, 407 (2018)
23. Elkhatib, D., Oyanedel-Craver, V.: A critical review of extraction and identification methods of microplastics in wastewater and drinking water. Environ. Sci. Technol. **54**(12), 7037–7049 (2020)
24. Fadare, O.O., Wan, B., Guo, L.H., Zhao, L.: Microplastics from consumer plastic food containers: are we consuming it? Chemosphere **253**, 126787 (2020)
25. Rainieri, S., Barranco, A.: Microplastics, a food safety issue? Trends Food Sci. Technol. **84**, 55–57 (2019)
26. Du, F., Cai, H., Zhang, Q., Chen, Q., Shi, H.: Microplastics in take-out food containers. J. Hazard. Mater. **399**, 122969 (2020)
27. Phillips, M.B., Bonner, T.H.: Occurrence and amount of microplastic ingested by fishes in watersheds of the Gulf of Mexico. Mar. Pollut. Bull. **100**, 264–269 (2015)

28. Murray, F., Cowie, P.R.: Plastic contamination in the decapod crustacean Nephrops norvegicus (Linnaeus, 1758). Mar. Pollut. Bull. **62**(6), 1207–1217 (2011)
29. Kim, J.S., Lee, H.J., Kim, S.K., Kim, H.J.: Global pattern of microplastics (MPs) in commercial food-grade salts: sea salt as an indicator of seawater MP pollution. Environ. Sci. Technol. **52**, 12819–12828 (2018)
30. Golwala, H., Zhang, X., Iskander, S.M., Smith, A.L.: Solid waste: an overlooked source of microplastics to the environment. Sci. Total Environ. 144581 (2021)
31. Conti, G.O., Ferrante, M., Banni, M., Favara, C., Nicolosi, I., Cristaldi, A., Fiore, M., Zuccarello, P.: Micro- and nano-plastics in edible fruit and vegetables. The first diet risks assessment for the general population. Environ. Res. **187**, 109677 (2020)
32. Van Cauwenberghe, L., Janssen, C.R.: Microplastics in bivalves cultured for human consumption. Environ. Pollut. **193**, 65–70 (2014)
33. Cho, Y., Shim, W.J., Jang, M., Han, G.M., Hong, S.H.: Abundance and characteristics of microplastics in market bivalves from South Korea. Environ. Pollut. **245**, 1107–1116 (2019)
34. Hernandez, L.M., Xu, E.G., Larsson, H.C., Tahara, R., Maisuria, V.B., Tufenkji, N.: Plastic teabags release billions of microparticles and nanoparticles into tea. Environ. Sci. Technol. **53**, 12300–12310 (2019)
35. Pivokonsky, M., Cermakova, L., Novotna, K., Peer, P., Cajthaml, T., Janda, V.: Occurrence of microplastics in raw and treated drinking water. Sci. Total Environ. **643**, 1644–1651 (2018)
36. Akanyange, S.N., Lyu, X., Li, X., Zhao, X., Zhang, Y., Crittenden, J.C., Anning, C., Chen, T., Jiang, T., Zhao, H.: Does microplastic really represent a threat? A review of the atmospheric contamination sources and potential impacts. Sci. Total Environ. 146020 (2021)
37. Rodríguez-Narvaez, O.M., Goonetilleke, A., Perez, L., Bandala, E.R.: Engineered technologies for the separation and degradation of microplastics in water: a review. Chem. Eng. J. 128692 (2021)
38. Mintenig, S.M., Löder, M.G.J., Primpke, S., Gerdts, G.: Low numbers of microplastics detected in drinking water from ground water sources. Sci. Total Environ. **648**, 631–635 (2019)
39. Schymanski, D., Goldbeck, C., Humpf, H.U., Fürst, P.: Analysis of microplastics in water by micro-Raman spectroscopy: release of plastic particles from different packaging into mineral water. Water Res. **129**, 154–162 (2018)
40. Ben, J., Mohamed, A., Muduli, K.: Optimizing bottle washer performance in cleaning returnable glass bottles for reuse in beverage packaging. Int. J. Adv. Sci. Technol. **29**, 8149–8159 (2020)
41. Weisser, J., Beer, I., Hufnagl, B., Hofmann, T., Lohninger, H., Ivleva, N.P., Glas, K.: From the well to the bottle: identifying sources of microplastics in mineral water. Water **13**, 841 (2021)
42. Kirstein, I.V., Hensel, F., Gomiero, A., Iordachescu, L., Vianello, A., Wittgren, H.B., Vollertsen, J.: Drinking plastics?–Quantification and qualification of microplastics in drinking water distribution systems by μFTIR and Py-GCMS. Water Res. **188**, 116519 (2021)
43. Winkler, A., Santo, N., Ortenzi, M.A., Bolzoni, E., Bacchetta, R., Tremolada, P.: Does mechanical stress cause microplastic release from plastic water bottles? Water Res. **166**, 115082 (2019)
44. Akoueson, F., Sheldon, L.M., Danopoulos, E., Morris, S., Hotten, J., Chapman, E., Li, J., Rotchell, J.M.: A preliminary analysis of microplastics in edible versus non-edible tissues from seafood samples. Environ. Pollut. **263**, 114452 (2020)
45. Barboza, L.G.A., Lopes, C., Oliveira, P., Bessa, F., Otero, V., Henriques, B., Raimundo, J., Caetano, M., Vale, C., Guilhermino, L.: Microplastics in wild fish from North East Atlantic Ocean and its potential for causing neurotoxic effects, lipid oxidative damage, and human health risks associated with ingestion exposure. Sci. Total Environ. **717**, 134625 (2020)
46. Hermabessiere, L., Paul-Pont, I., Cassone, A.L., Himber, C., Receveur, J., Jezequel, R., El Rakwe, M., Rinnert, E., Rivière, G., Lambert, C., Huvet, A.: Microplastic contamination and pollutant levels in mussels and cockles collected along the channel coasts. Environ. Pollut. **250**, 807–819 (2019)
47. Li, D., Shi, Y., Yang, L., Xiao, L., Kehoe, D.K., Gun'ko, Y.K., Boland, J.J., Wang, J.J.: Microplastic release from the degradation of polypropylene feeding bottles during infant formula preparation. Nat. Food **1**, 746–754 (2020)

48. Mohamed Nor, N.H., Kooi, M., Diepens, N.J., Koelmans, A.A.: Lifetime accumulation of microplastic in children and adults. Environ. Sci. Technol. **55**, 5084–5096 (2021)
49. Revel, M., Châtel, A., Mouneyrac, C.: Micro (nano) plastics: a threat to human health? Curr. Opin. Environ. Sci. Health **1**, 17–23 (2018)
50. Cox, K.D., Covernton, G.A., Davies, H.L., Dower, J.F., Juanes, F., Dudas, S.E.: Human consumption of microplastics. Environ. Sci. Technol. **53**, 7068–7074 (2019)
51. Prata, J.C., da Costa, J.P., Lopes, I., Duarte, A.C., Rocha-Santos, T.: Environmental exposure to microplastics: an overview on possible human health effects. Sci. Total Environ. **702**, 134455 (2020)
52. Kwon, J.H., Kim, J.W., Pham, T.D., Tarafdar, A., Hong, S., Chun, S.H., Lee, S.H., Kang, D.Y., Kim, J.Y., Kim, S.B., Jung, J.: Microplastics in food: a review on analytical methods and challenges. Int. J. Environ. Res. Public Health **17**, 6710 (2020)
53. Wang, C., Xian, Z., Jin, X., Liang, S., Chen, Z., Pan, B., Wu, B., Ok, Y.S., Gu, C.: Photo-aging of polyvinyl chloride microplastic in the presence of natural organic acids. Water Res. **183**, 116082 (2020)
54. Wang, C., Zhao, J., Xing, B.: Environmental source, fate, and toxicity of microplastics. J. Hazard. Mater. 124357 (2020)
55. Schwabl, P., Köppel, S., Königshofer, P., Bucsics, T., Trauner, M., Reiberger, T., Liebmann, B.: Detection of various microplastics in human stool: a prospective case series. Ann. Intern. Med. **171**, 453–457 (2019)
56. Senathirajah, K., Attwood, S., Bhagwat, G., Carbery, M., Wilson, S., Palanisami, T.: Estimation of the mass of microplastics ingested—a pivotal first step towards human health risk assessment. J. Hazard. Mater. **404**, 124004 (2021)
57. Vethaak, A.D., Legler, J.: Microplastics and human health. Science **371**, 672–674 (2021)
58. Schoppa, H.R.: How microplastic in the environment influences the human health (2021)
59. Hammer, J., Kraak, M.H., Parsons, J.R.: Plastics in the marine environment: the dark side of a modern gift. In: Reviews of Environmental Contamination and Toxicology, pp. 1–44 (2012)
60. Lithner, D., Larsson, Å., Dave, G.: Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition. Sci. Total Environ. **409**, 3309–3324 (2011)
61. Waring, R.H., Harris, R.M., Mitchell, S.C.: Plastic contamination of the food chain: a threat to human health? Maturitas **115**, 64–68 (2018)
62. Karbalaei, S., Hanachi, P., Walker, T.R., Cole, M.: Occurrence, sources, human health impacts and mitigation of microplastic pollution. Environ. Sci. Pollut. Res. **25**(36), 36046–36063 (2018)
63. Proshad, R., Kormoker, T., Islam, M.S., Haque, M.A., Rahman, M.M., Mithu, M.M.R.: Toxic effects of plastic on human health and environment: a consequences of health risk assessment in Bangladesh. Int. J. Health **6**(1), 1–5 (2018)
64. Ahmad, J., Naeem, S., Ahmad, M., Usman, A.R., Al-Wabel, M.I.: A critical review on organic micropollutants contamination in wastewater and removal through carbon nanotubes. J. Environ. Manage. **246**, 214–228 (2019)
65. Lee, C., Jung, J., Pawar, R.R., Kim, M., Lee, S.M.: Arsenate and phosphate removal from water using Fe-sericite composite beads in batch and fixed-bed systems. J. Ind. Eng. Chem. **47**, 375–383 (2017)
66. Sawant, S.Y., Han, T.H., Ansari, S.A., Shim, J.H., Nguyen, A.T.N., Shim, J.J., Cho, M.H.: A metal-free and non-precious multifunctional 3D carbon foam for high-energy density supercapacitors and enhanced power generation in microbial fuel cells. J. Ind. Eng. Chem. **60**, 431–440 (2018)
67. Foroutan, R., Mohammadi, R., Adeleye, A.S., Farjadfard, S., Esvandi, Z., Arfaeinia, H., Sorial, G.A., Ramavandi, B., Sahebi, S.: Efficient arsenic (V) removal from contaminated water using natural clay and clay composite adsorbents. Environ. Sci. Pollut. Res. **26**(29), 29748–29762 (2019)
68. Srinivasan, R.: Advances in application of natural clay and its composites in removal of biological, organic, and inorganic contaminants from drinking water. Adv. Mater. Sci. Eng. **2011** (2011)

69. Li, M., He, L., Zhang, X., Rong, H., Tong, M.: Different surface charged plastic particles have different cotransport behaviors with kaolinite particles in porous media. Environ. Pollut. **267**, 115534 (2020)
70. Shen, M., Hu, T., Huang, W., Song, B., Zeng, G., Zhang, Y.: Removal of microplastics from wastewater with aluminosilicate filter media and their surfactant-modified products: performance, mechanism and utilization. Chem. Eng. J. **421**, 129918 (2021)
71. Besseling, E., Quik, J.T., Sun, M., Koelmans, A.A.: Fate of nano-and microplastic in freshwater systems: a modeling study. Environ. Pollut. **220**, 540–548 (2017)
72. Wagner, M., Lambert, S.: Freshwater Microplastics: Emerging Environmental Contaminants?, p. 303. Springer Nature (2018)
73. Pivokonský, M., Pivokonská, L., Novotná, K., Čermáková, L., Klimtová, M.: Occurrence and fate of microplastics at two different drinking water treatment plants within a river catchment. Sci. Total Environ. **741**, 140236 (2020)
74. Brewer, A., Dror, I., Berkowitz, B.: The mobility of plastic nanoparticles in aqueous and soil environments: a critical review. ACS ES&T Water **1**(1), 48–57 (2020)
75. Sharma, V.K., Ma, X., Guo, B., Zhang, K.: Environmental factors-mediated behavior of microplastics and nanoplastics in water: a review. Chemosphere **271**, 129597 (2021)
76. Shiu, R.F., Vazquez, C.I., Tsai, Y.Y., Torres, G.V., Chen, C.S., Santschi, P.H., Quigg, A., Chin, W.C.: Nano-plastics induce aquatic particulate organic matter (microgels) formation. Sci. Total Environ. **706**, 135681 (2020)
77. Chen, N., Fang, G., Liu, G., Zhou, D., Gao, J., Gu, C.: The degradation of diethyl phthalate by reduced smectite clays and dissolved oxygen. Chem. Eng. J. **355**, 247–254 (2019)
78. Ding, L., Yu, X., Guo, X., Zhang, Y., Ouyang, Z., Liu, P., Zhang, C., Wang, T., Jia, H., Zhu, L.: The photodegradation processes and mechanisms of polyvinyl chloride and polyethylene terephthalate microplastic in aquatic environments: important role of clay minerals. Water Res. **208**, 117879 (2022)
79. Zhu, K., Jia, H., Zhao, S., Xia, T., Guo, X., Wang, T., Zhu, L.: Formation of environmentally persistent free radicals on microplastics under light irradiation. Environ. Sci. Technol. **53**(14), 8177–8186 (2019)
80. Xu, L., Li, H., Mitch, W.A., Tao, S., Zhu, D.: Enhanced phototransformation of tetracycline at smectite clay surfaces under simulated sunlight via a Lewis-base catalyzed alkalization mechanism. Environ. Sci. Technol. **53**(2), 710–718 (2018)
81. Xi, Y., Mallavarapu, M., Naidu, R.: Preparation, characterization of surfactants modified clay minerals and nitrate adsorption. Appl. Clay Sci. **48**(1–2), 92–96 (2010)
82. Seidensticker, S., Grathwohl, P., Lamprecht, J., Zarfl, C.: A combined experimental and modeling study to evaluate pH-dependent sorption of polar and non-polar compounds to polyethylene and polystyrene microplastics. Environ. Sci. Eur. **30**(1), 1–12 (2018)
83. Zhang, Y., Luo, Y., Guo, X., Xia, T., Wang, T., Jia, H., Zhu, L.: Charge mediated interaction of polystyrene nanoplastic (PSNP) with minerals in aqueous phase. Water Res. **178**, 115861 (2020)
84. Singh, N., Khandelwal, N., Ganie, Z.A., Tiwari, E., Darbha, G.K.: Eco-friendly magnetic biochar: an effective trap for nanoplastics of varying surface functionality and size in the aqueous environment. Chem. Eng. J. **418**, 129405 (2021)
85. Huang, Z., Bu, J., Wang, H.: Application of two modified kaolin materials in removing microplastics from water. J. Mater. Cycles Waste Manag. **24**(4), 1460–1475 (2022)
86. Singh, N., Tiwari, E., Khandelwal, N., Darbha, G.K.: Understanding the stability of nanoplastics in aqueous environments: effect of ionic strength, temperature, dissolved organic matter, clay, and heavy metals. Environ. Sci. Nano **6**(10), 2968–2976 (2019)

Antimicrobial Applications of Clay Nanotube-Based Composites

Shoomaila Latif, Muhammad Imran, Memoona Ahmad, Aisha Urooj, and Muhammad Abubakar Siddique

Abstract In recent years, there has been growing concern about the effect of carbon nanotubes on human health and the environment because of their toxic potential nature. These carbon nanotubes are synthetic in origin, non-biodegradable, and non-biocompatible, hence harmful effects and environmental hazards. To overcome these drawbacks, green nanotechnology is one of the promising technologies that aims and advancing environmentally safe and less harmful nanoproducts. Thus, clay nanotubes, nanocomposites, and nanopowders are emerging trendsetters in green nanotechnology. The clays are natural materials that possess great antimicrobial activity and proven biocompatibility and are easily available at very low prices. The important clays are halloysite (HNT) which are naturally occurring clays of aluminosilicate and have been investigated as having excellent antimicrobial applications in medicine and clinical studies. Antimicrobial activity is a collective process of all such active principles which inhibit, prevent, and destroy bacteria, microorganisms, microbial colonies, etc., and industries need materials for doing such antimicrobial activity, preventing infections, and for the safety of their products. Keeping in view recent trends, in this chapter, various clay nanotube-based composites will be discussed with special emphasis on their antimicrobial applications.

Keywords Nanomaterials · Carbon nanotubes · Biomedical applications

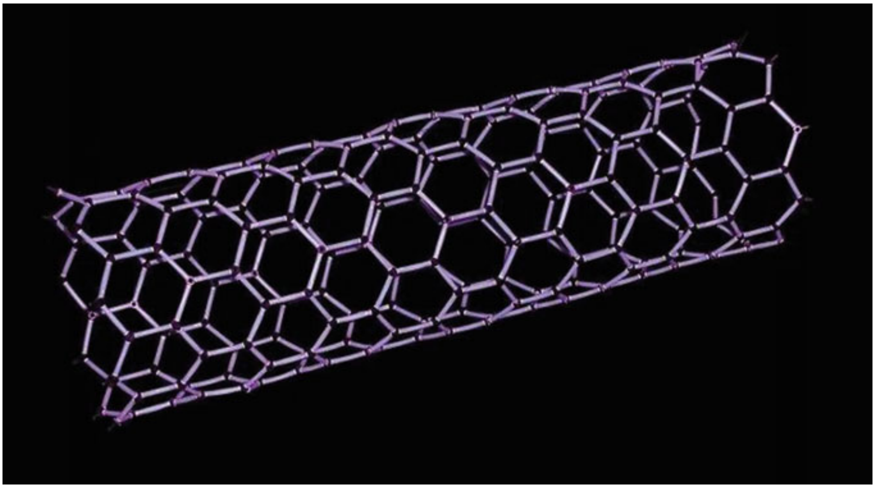
---

S. Latif (✉) · M. Ahmad · A. Urooj · M. A. Siddique
School of Physical Sciences, University of the Punjab, Lahore, Pakistan
e-mail: shoomaila.sps@pu.edu.pk

M. Imran
Centre for Inorganic Chemistry, School of Chemistry, University of the Punjab, Lahore, Pakistan

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_19

1 Introduction



Clay nanotubes or HNTs (Halloysite nanotubes) could be mined from different mineral deposits because these exist naturally all over the world. That is why these are easily accessible and very cost-effective nanomaterials [30]. These possess chemical similarities with kaolin clay with a two-layered aluminosilicate structure and tubular features [11]. Their inner diameter is about 15–50 nm, and their length is around 100–2000 nm. They possess huge surface areas which are why, they could be easily coated and loaded with various materials like biomacromolecules, drugs, and organic compounds. It is only due to their larger surface areas that a wide range of active agents like drugs, antibiotics, biological molecules, cancer drugs, marine biocides, and antimicrobial agents could be easily entrapped in not only their mineral inner lumen but also in void spaces of aluminosilicate and shells [24]. is also their excellent property that these clay nanotubes are non-cytotoxic over various cell types which include dermal fibroblasts, chondrocytes, stem cells, osteoblasts, etc. [36].

It has been studied through a complete biocompatibility study in the model of rat dermal that clay nanotubes do not incite host immune response or cytotoxic response. Therefore, due to their high level of cytocompatibility, clay nanotubes represent themselves as the ideal candidate to be utilized for polymer additives, templates, and drug delivery systems in nanotechnology [9]. Due to their great biocompatibility, clay nanotubes have been widely used as antimicrobials by incorporating antimicrobial properties to them.

Antimicrobial properties have been imparted to clay nanotube composites by various methods which include loading antimicrobial organic compounds like povidone, green iodine, amoxicillin, chlorhexidine, etc., inside clay lumen. Other methods include a coating of clay nanotubes with metal nanoparticles like silver and copper to make them antimicrobial nanocomposites [2]. These clay nanotube composites possess antimicrobial agents that provide a variety of antimicrobial applications in various fields like health and medicine, the food industry, clinics and hospitals, bone and tissue engineering, wound dressing, food packaging and food contact materials, dentistry, filtration membranes, and surface disinfectants, etc.

The objectives of this chapter include signifying how advancement has come in clay nanotube composites use and how various methods have been adopted with time to impart excellent antimicrobial properties to clay nanotube composites [28]. It has been highlighted that those organic compounds loading methods that have been used in HNTs to impart antimicrobial properties to them were slow in drug release. But with advancement, various methods have been developed which include the coating of HNTs with metal nanoparticles which are more efficient than old methods, and these also stand against the limitations of old methods [32]. This chapter aims to find out and highlight not only the antimicrobial applications of clay nanotube composites but also to demonstrate the ways through which these antimicrobial properties have been imparted to clay nanotube composites.

2 Structure and Chemical Composition of Clay Nanotubes

Clay nanotube is composed of aluminosilicate double layer which occurs in hollow spherical or tubular in structure a large amount clay silicate which contains thin plates. HNTs typically originate in soils formed from glass and volcanic ash such as volcanic deposits [17]. It is present in the order of Andisol soil and is also called a clay mineral. The empirical formula of aluminosilicate mineral is $Al_2Si_2O_5$ $(OH)_4$ nH_2O. Halloysite clay nanotubes (HNTs) are occurring naturally in the tubular nanostructure, formed by rolling sheets of aluminosilicate kaolin several times. On the surface of the clay nanotube, the siloxane and alumina groups help in the hydrogen bonding formation on its surface with the materials of biomolecules [14]. It consists of aluminium (20.90%), silicon (21.76%), hydrogen (1.56%), and oxygen (55.78%). Nano-clays are layered silicate nanomaterials.

In the chemical composition and morphology of nanoparticles, HNTs polymer composites originate in various divisions including halloysite, hectorite, bentonite, and montmorillonite [8]. HNTs clay nanotubes are usually formed by hydrothermal alteration of aluminosilicate natural resources. It has 1 1 m in length, 50–80 nm of its outer diameter, and the lumen diameter is almost 10–15 nm. In clay, nanotube (HNT) hydrogen bonding formed in the aluminium and siloxane groups on the HNT surface of biomaterials. Omaliusd Halloy is the first person who discovered clay nanotube and named it halloysite after its discovery**,** the mineral in Belgium. In1826, Berthier describes the clay nanotube first.

Clay nanotube, also called halloysite, is abundant and economical. These are found in natural deposits in tonnes of almost tens of thousands. Chemically HNTs are comparably similar to another type of clay mineral which is kaoline. In HNT, in tubes, the aluminosilicate sheets are rolled while a platy particle leads to kaolin. Halloysite reveals its dimensions on the nanoscale which shows nanotubular geometry [12]. Clay nanotubes have nanotubular arrays having different regions in their structure.

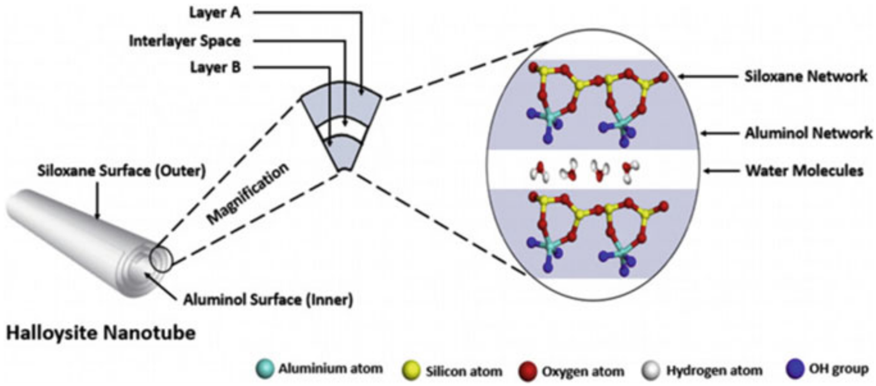


Fig. 1 Structure and chemical composition of clay nanotube-based composites (reproduced with permission under license no. 5443490776479 from the source [9])

Clay nanotube has two important functional groups which have different pH ranges and surface charges, one is eternal (Al-OH) surface, and the other one is external (Si-O-Si) surfaces.

Halloysite clay is a tubular structure nanotube which contains inner lumen with a positive charge and 8.5 pH. While, it has an outer lumen surface with a negative charge and 1.5 pH. Nifedipine, Furosemide, and Dexamethasone are negatively charged molecules [6]. These molecules have charge differences in their surfaces, and due to this reason, they can be loaded inside the clay lumen. The negatively charged outer surfaces of tubules are adhering to charge differences. Clay nanotubes are also known as nanocontainers due to their functional groups which are used in their inner and outer surfaces [1]. Nanocontainers are used for controlled release by loading molecules like enzymes and drugs into polymers that are bioactive apart from their solubility [25]. These bioactive molecules are loaded into clay nanotube-based composites through a variety of mechanisms like tubular entrapment, adsorption, and intercalation. The structure and chemical composition of HNT are shown Fig. 1.

2.1 Composition of Antimicrobial Clay Nanotube-Based Composites

In HNTs nanotubes, there are two different accepted techniques are generally used to teach antimicrobial properties. First is HNTs lumen loading of organic materials occurs and adsorption takes place on the exterior surface, and the second one is external grafting [40]. There are various methods of loading molecules into halloysite nanotubes, and these are given below.

2.1.1 Adsorption

In the thermodynamic equilibrium, the process of adsorption involves stirring of drugs and for one-day loading of halloysite nanotube. Oven drying and centrifugation processes are used to form loaded drug composites of polymer halloysite. The rate of equilibrium absorption is generally described and identified by an isotherm. Langmuir isotherm is obeyed according to the cationic drug (loading drugs) over halloysite nanotube through adsorption phenomena [22]. Diclofenac sodium exhibited significant adsorption and is also a loading drug over the surface of poly-ionic minerals [39].

On the contrary, in fewer concentrations of drug solution, the Langmuir adsorption theory of isotherm is not constantly correct. In HNTs, the binding camber of diclofenac sodium is shaped abnormally showing that multilayers are occurring in its adsorption. In HNTs surface, adsorption phenomena have been exhibited by approving various types of experiments [27]. In this mechanism, clay nanotube composites act as a nano-adsorbent in which the absorptions of cationic molecules through pollutants treat water waste material.

2.1.2 Intercalation

HNT clay nanocomposites can be used to intercalate some bioactive materials of organic as well as inorganic molecules because they are the materials of the interlayer [29]. In the process of d001 spacing 0.3–0.5 nm expands between the layers when the bioactive molecules are entering the interlayer space. The materials of intercalating clay nanotube form significant interactions of dipole and hydrogen bonding when interacting with tetrahedral silicone and silica sheets. Furthermore, HNTs are intercalated by the functional group of anionic interrelate with layers of alumina for example dimethyl sulfoxide, potassium acetate, amides, aniline, hydrazine, formamide, etc.

By increasing temperature, the halloysite nanotubes are dehydrated due to the absence of strong hydrogen bonding that causes low intercalation potential. The intercalation fact is associated with the interlayer water; the exchange of water molecules between wall layers of halloysite clay nanotube is the demand of intercalation. The drawback of this technique is the partial space between the wall layers of halloysite composite from loaded to prevent increasing molecular weight. Subsequently, in these applications, it might be accommodated by the use of smaller materials including drugs and corrosion inhibitors.

2.1.3 Tubular Entrapment

Tubular entrapment is mainly the well-known loading of HNT composites also called as vacuum method. This technique opposite to intercalation allows for storing the different substances in the halloysite composite (HNT) lumen. Tubular entrapment has two different techniques; the general process of this technique is as follows.

The gerneral process of tubular entrapment technique is stirring the dried halloysite clay nanotube (HNT) with a highly concentrated solution of selected molecules. The walls of HNT have excellent solubility with less viscous solvents. This solubility is particularly excellent for bioactive molecules because organic substance contains desirable ethanol and acetone. It has also identified that negatively charged bioactive solvents have greater dielectric constant which results considerable quantity of drug loading. A homogenous mixture is formed from the suspension which is shifted through evacuating various times to a vacuum jar via a vacuum pump. In this process of vacuum, from the balanced nanotube composites, HNTs air is removed showing the sign of fizzing of minor solution of the lumen. Within 10–30 min of the process of vacuum, the suspended medium should remove air by atmospheric pressure by replacing air with a desirable substance.

This technique is repeated several times to ensure that bioactive molecular solutions are present in HNTs lumen. HNTs composites lumens have almost 15 nm diameter and 10–15 wt.% molecules of biomaterials and are very close to theoretical estimates. In the cycle of the vacuum process, attached bioactive molecules are removed by centrifugation of halloysite composite suspension weakly. By repeating the washing process, it is clear that nanotube composites are fully loaded with the most wanted substance which has active sites of biomolecules.

In the second procedure, targeted bioactive molecules of bioactive materials are mixed with HNT composites in equal amounts. As an alternative to diffusion, in this method, the final mixture is a thick paste that is cycled between atmospheric pressure and vacuum two to three times. The resultant product of the mixture has active biomolecules in a dried vacuum. In HNTs, the maximum amount of targeted active biomolecules latter method is used to avoid solution wastage and bioactive molecules.

2.1.4 Halloysite Nanotubes or Polymer Composites

Halloysite nanotube composites are more hydrophobic than layered silicates and other nano-silica because of their lesser density at the outer surface area of hydroxyl groups so the interaction of tube–tube halloysite is comparatively weak. There are many methods applied for the formation of polymer composites commonly including functional methods like melt blending, solvent casting, electrospinning, etc. Additionally, clay nanotube (HNT) or polymer composites can be formed by compression moulding, in-situ polymerization, coagulation, hydrogel preparation, injection moulding, and deposition of polycations and HNT.

Clay nanotube-based composites are synthesized by several economical methods. The way of method was used to enhance HNT distribution into a polymeric matrix with enhanced interfacial interaction. Due to polymer distribution, some basic properties of clay nanotubes are affected which include HNT in the polymer matrix, thermomechanical, and microstructure. The homogeneous dispersion of polymer composites into its matrix than aggregates promotes some microstructural features. The formation of improved compression moulding and water-assisted injection mouldings technology has some morphological properties of HNT clay nanotube or polypropylene (HNT/PP) nanocomposites. With the improvement of the mechanical behaviour of clay nanotube (HNT)-based composites, the number of polymer composites is increased in a polymeric matrix [15]. The increasing amount of polymer composites shows more mechanical characteristics due to intrinsic stiffness, its increasing ratio, and uniformed distribution of halloysite nanotube into the matrix of polymeric.

The enhanced tensile modulus and flexural are considered when a consistently HNTs distribution is included in polylactide (PLA) matrices. The enhancement may be ascribed to the rigidity improvement of the nanotube-based composites by HNTs, allowing at the interface of clay nanotube advanced stress transfer. Therefore, the polymeric nanocomposites have no remarkable improvement in their tensile strength observed due to weak interference between HNTs surface and PLA matrix. On the other hand, by applying the quaternary ammonium salt to treat with HNT nanotube (modified-HNT) the advantageous interface of PLA matrix and polymer composites is observed. Young's modulus and mechanical strength of clay nanotube-based composites improved much more advanced than an unmodified nanotube-based composite of HNT or PLA.

The mechanical behaviour of polyvinyl alcohol-HNT was observed with nanotube-based composites with increased tensile strength and its elongation up to 7.5 wt.% loading HNT. Furthermore, by strengthening effects of clay nanotube with better mechanical behaviour thermal stability and flame retardancy have been reported.

For unique polymeric nanotube-based composites to expand some new horizons in biomedical applications the major characteristics of HNTs act as a carrier for conductive filler and controlled delivery release. Designing and engineering biomedical yields clay nanocomposites allow its flexibility. Polyacrylic acid (PAA) or clay hydrogel composites are used as an absorbent in water waste for the removal of ammonia. HNT clay hybrid beads are used as alginates and are very efficient to eliminate methylene blue. In these practical applications, nano-, polymer-based composites are used for the removal of dye.

3 Methods for Preparing Clay Nanotube-Based Composites

Clay nanotubes possess unique properties which make them disperse more eagerly in polymeric matric structures as compared to platy clay-like montmorillonite and Kaolin. HNTs possess hydrophilic properties which make them easily disperse in systems of polar polymetric which include polyvinyl alcohol, polyamides, biopolymers, and polymethylmethacrylate. However, clay nanotubes also possess compatibility with systems of non-polymers like polylactic acid and polypropylene utilizing surface-compatible agents with it. There are various methods available for preparing HNT or polymer composites [10].

3.1 Melt Blending

It is generally utilized functional method for preparing clay nanotube composites. In this technique, the polymer is first melted and allowed to combine with intercalated clay's required quantity via an extruder [18]. This process is done utilizing inert gases like neon, argon, or nitrogen. The dried polymer is mixed with some intercalant and heated in a mixer where it is subjected to some shear sufficient to make the desired polymer of clay nanocomposite. It is an environmentally benign and friendly process which is why found various applications in industries.

3.2 Solvent Casting

Solvent casting is another standard technique for preparing HNT nanocomposites in a well-dispersed polymer mixture. In this, HNTs are cast and then allowed to be dried for creating the polymer nanocomposite films. It is a process in which HNT nanocomposite has been prepared by dissolving the polymer into volatile solvents for getting a homogenous solution possessing low viscosity. The solution could be either spread over the substrate or cast into the mould. Then, polymer film is allowed to adhere to the mould by drawing off the solvent from it. This technique is advantageous because films of solvent cast dried by themselves without using any external factor like mechanical or thermal stress. Many additives could also be introduced into the polymer-solvent solution. The polymer films produced through this method possess great optical clarity and thickness which has homogenous distribution [38].

3.3 Electrospinning

It is also another famous method for producing HNT nanocomposites. The electrospinning process includes an electrodynamic process in which a liquid droplet is allowed to be electrified for generating a jet which is followed by elongation and stretching to produce fibres [42]. In this process, the polymer melt is charged and ejected into the spinneret utilizing the high voltage of an electric field for solidifying the coagulate to create a filament. This process is suited particularly for producing complex and large molecules, and it ensures that no solvent is left over in the final product [4].

4 Imparting of Antimicrobial Properties to Clay Nanotube-Based Composites

For imparting antimicrobial properties to clay nanotubes, various approaches have been used. These include organic molecules loading inside the lumen of clay-like halloysite and then adsorption of it over the external surface. The other approach which is generally accepted is outside grafting. Nowadays, grafting of clay nanotubes with metal nanoparticles like Ag and Cu nanoparticles which act as antimicrobial agents is proved as a very effective method to give antimicrobial applications to HNTs. The clay nanotube composites which have been incorporated with antimicrobial properties by loading antimicrobial agents in it have been used for various purposes like in wound dressings, bone regeneration, nanofibres, and the electrospun membrane.

4.1 Organic Compounds Loading Inside Clay Nanotubes

For the loading of antimicrobial agents like organic compounds inside the clay nanotubes composites and their adsorption on clay/halloysite, the two techniques assist it. These techniques are vacuuming and sonication which assists while stirring this drug solution of antimicrobial agents. The efficiency with which antimicrobial agents have been loaded inside clay nanotube depends on the size, charge, and procedure of the overall process. Some of the antimicrobial agents which have been widely used for loading inside clay nanotubes are green iodine, gentamicin sulphate, vancomycin, povidone-iodine, tetracycline, doxycycline, potassium clavulanate, amoxicillin, brilliant green, and chlorhexidine [23]. These all-antimicrobial agents have been loaded inside clay nanotube composites using vacuum and sonication. For having excellent antimicrobial properties in clay nanotube-based composites, the kinetics parameter of drug release is the most crucial one. The commonly used and practical antibacterial medicines are amoxicillin, anionic povidone-iodine, and cationic chlorhexidine [39].

4.1.1 Loading of Chlorhexidine Gluconate Inside HNT Composite

The organic compound, chlorhexidine gluconate although possesses a positive charge but still could be easily loaded within clay nanotube composites. The loading of this organic compound within HNT shows only 25% of its sustained release within the first hour. However, this drug shows 75% of its release when it is present in its original untreated micro powder as an unloaded drug. That is why chlorhexidine gluconate has been introduced into the coating of cotton fabric for its loading within clay nanotubes because it helps to improve the antimicrobial activities of chlorhexidine gluconate without the need of using the silver particles in it.

It has been observed that the loading of chlorhexidine gluconate with the help of cotton fabric coating increases its antimicrobial property and shows a reduction of bacteria, *Staphylococcus aureus, Pseudomonas, and Escherichia Coli* by 98%. It has shown its antimicrobial activity by 90% even if it gets washed 20 times because of chlorhexidine gluconate's slow release from clay nanotubes.

4.1.2 Loading of Amoxicillin and Povidone-Iodine Inside HNT Composite

Antimicrobial compounds amoxicillin and povidone-iodine have also been commonly loaded within HNT composites and possess a slow rate of drug release. These drugs have been first prepared in the form of their mixture for loading within HNT. The saturated solution of amoxicillin (50 mg/ml) and povidone-iodine (80 mg/ml) has been added into HNT as drug solutions and then allowed to be stirred for obtaining their homogenous suspensions. These solution suspensions are then placed within a vacuum for one hour in three cycles for ensuring their maximum loading inside HNT. This loaded clay nanotube is allowed to be washed twice for removing external/excess drugs if present inside the vacuum desiccator. It is placed overnight to make it in powder form so that these powder formulations could be stockpiled for their long-time usage and in the future, easily dispersed by mechanical stirring in water before usage [39].

The efficiency of loading of these drugs is then determined by using TGA (Thermogravimetric Analysis), and their release efficiency has been analysed with the help of a UV-VIS spectrophotometer on 227 nm for amoxicillin and 224 nm for povidone-iodine. The curves of TGA show 8.3 and 7.6 wt.% of amoxicillin and povidone-iodine loading inside HNT. It has been identified that the loading of these drugs could be enhanced by clay nanotube lumen enlarging using sulfuric acid for etching inner alumina. These formulations are found efficient for *Escherichia Coli* and *Staphylococcus aureus* inhibition for a whole one week and their extended-release was found as 6–20 h. These types of formulations are found very effective for sprays in which clay nanotubes have been loaded with 3–5 wt.% antiseptics, and these form a thin coating after spraying with extended antimicrobial activity [39].

4.2 Utilization of Metals as Antimicrobials

It has been identified that organic antiseptics loading inside HNTs has its limitations because of its slow drug release. The pathogen's exposure to low concentrations of drugs progressively could become a risk factor in selecting drug resilient strains, and this factor could not be ignored in any case. That is why, new strategies need to get adapted, and this problem's possible solution is hidden in the utilization of metal nanoparticles as antimicrobial agents for producing the antimicrobial composites [3].

It has been studied previously that clay nanotubes (HNTs) possess huge surface area, which is why could be loaded with various materials like polymers, biomacromolecules, and drugs for extended and sustained releases. For fabricating uniform nanomaterials with a high yield in nanotechnology, it is important to know the antibacterial response of that nanotube and whether its nanofabrication procedures are cost-effective or not. It has been observed throughout history that metals are utilized as antimicrobials, and these are proven effective today against bacteria. However, advancements have been continuing to come with time in the synthesis of metallic nanoparticles and give rise to new antimicrobial fabrication technologies with age [5].

4.2.1 Advancement in Metal Nanoparticles Depositions Over HNTs

There are various methods developed with time to deposit the metal nanoparticles over the inner lumen and outer surfaces of clay nanotubes by the use of particular metallic salt or compound with it in a multistep chemical reaction and at high calcination temperature. The utilization of metal as a support system with HNTs includes many advantages like large surface area, low cost, scale nanometre tubular morphology, and availability. These have been utilized as antimicrobials from Hippocrates' time till today and are very effective. In past, Ag electric colloids and synthetic antibiotics were common methods in antimicrobial therapies.

Currently, the processes of electrochemical nano-assembly perform a new role in depositing the metal nanoparticles over clay nanotubes for giving them antimicrobial features. However, in past, fabricating methods of clay nanotubes, metallization involve multistep processes which comprise organic compounds, high temperatures, metal salts, and reducing agents to gain surface modifications in HNTs.

There are Cu and Ag particle technologies in wound dressings, disinfecting sprays, and hospitals. It is because metal nanoparticles like Ag and Cu have displayed extreme toxic behaviour towards bacteria even though at many low concentrations. It was studied that these transition metals possess the ability to disrupt bacterial electron transport and respiration systems upon their absorption within bacterial cells. These transition metals are being incorporated into the inert materials of polymers for preventing infections. Recently, Ag use has been increased as an antimicrobial agent within textile industries for antimicrobial washes and polymers [3].

4.2.2 Copper (Cu) Nanoparticles as Antimicrobial Agents

The Cu nanoparticles act as redox-active metals which oxidize themselves during their interaction with bacterial cell membranes. The toxicity which has been induced by Cu involves multiple mechanisms such as ROS formation through free ions of Cu where cuprous and cupric ions participate in redox reactions. It has been studied that Cu^{2+} ions possess the ability to reduce into Cu^{+} in reducing agents' presence to catalyse the hydroxyl radicals' formation by hydrogen peroxide. These produced hydroxyl radicals are extremely reactive and detrimental to processes like protein oxidation and cellular molecules of bacterial cells [5].

4.2.3 Silver (Ag) Nanoparticles as Antimicrobial Agents

In the case of Ag nanoparticles, these anchor within bacterial cells penetrates them and does structural damage to bacterial cells which eventually causes their cell death. It happens due to Ag ions released from Ag nanoparticles, and it has also been observed under electron spin resonance spectroscopy that these metals also produce free radicals in bacterial cells present. These produced free radicals possess the ability to make bacterial cell membranes porous and lead to cell death [3].

4.2.4 Clay Nanotubes Nanostructured Coating with Antimicrobial Metals

Clay or halloysite nanotubes could be utilized as a substrate material in doing nanostructured coating over it by metals as antimicrobial agents. For this purpose, electrolysis techniques have been identified as novel procedures for depositing metal nanoparticles over clay nanotube surfaces. Moreover, metal clay nanotubes showing antimicrobial activity have also been monitored against gram-positive and gram-negative bacteria with the help of a spectrophotometer. Antimicrobial applications have been given by such clay nanotubes which possess modified surfaces with pure Cu and Ag nanoparticles using electrolysis. Generally, the process of coating clay nanotubes with metals has been done in distilled water containing mixed HNTs in it. The constant direct current has been applied to electrodes of metals for synthesizing the metal nanoparticles and facilitating these metal nanoparticles' deposition over clay nanotube surfaces. The detailed fabrication processes of these clay nanotube coatings with various transition metals for giving antimicrobial properties to them are given below.

4.2.5 Silver-Clay Nanotube (Ag-HNT) Synthesis

For preparing Ag nanoparticle coated clay nanotube composites, these Ag metal electrodes have been placed within 500 millilitres of distilled water by keeping a distance of 0.5 inches between these metal electrodes. This mixture was then heated over 95 °C, and this whole setup has been connected to an outside power supply of direct current. Further, 300 mg HNTs were also added to the heated mixture by constantly stirring this mixture with the help of a magnetic stirrer. After this, a direct constant current has been applied to this mixture for 40 min by keeping the current at 30 V. Then, power supply was disconnected when 40 min were passed, and this mixture is allowed to be centrifuged. The supernatant obtained was decanted and an

Ag-clay nanotube which has been achieved as the final product then dried for 24 h at 60 °C. The variations in the use of HNTs mixture, distilled water, and applied direct current period could be used to check the rate of antimicrobial activity of the same metal nanoparticle coated clay nanotube.

4.2.6 Copper-Clay Nanotube (Cu-HNT) Synthesis

The same method has been used for preparing the Cu nanoparticle coated clay nanotube composites. Like Ag metal electrodes, Cu electrodes were also placed within 500 mL of distilled water by keeping the distance of 0.5 inches between these metal electrodes. This solution was then heated over 95 °C, and this whole setup has been connected to the outside power supply of direct current. Further, 300 mg HNTs were also added to the heated solution by constantly stirring this mixture with the help of a magnetic stirrer. After this, direct constant voltage has been applied to this solution for 40 min by keeping the current at 240 V. Then, power supply was disconnected when 40 min were passed, and this mixture is allowed to centrifuge. The supernatant obtained was centrifuged and then decanted. The Cu-clay nanotube which has been achieved as the final product is then dried for 24 h at 60 °C. The variations in the use of HNTs mixture, distilled water, and applied direct current time could also be used to check the rate of antimicrobial activity of Cu metal nanoparticle coated clay nanotube.

4.2.7 Surface Modification of HNT

The samples of Cu-HNT and Ag-HNT have proved that the method of electrochemical deposition is a very effective way to make HNT-meta composites. It has been observed that the deposition of metal is based on the time taken for the electrolysis process and HNTs concentration utilized. For instance, Ag-HNT which has been fabricated by using 300 mg HNT possesses a much higher weight% of Ag as compared to Ag-HNT which has been fabricated using 5 g HNT. Similarly, the fabricated Cu-HNT composite at 300 mg possesses a higher Cu % weight compared with fabricated Cu-HNT at 5 g. In the same way, the electrolysis which has been done under increased time amount would produce a meta-HNT composite with higher metal % weight deposition on their surfaces.

It has also been observed that Cu nanoparticles show clusters having irregular geometries and Ag nanoparticles are spherical mostly. It is because the voltage amount applied has affected the particle size of these metals. The results of TEM have shown that there are small particle metal sizes observed by applying a lower amount of voltage and with increasing voltage levels, the nanoparticle sizes, and their deposition on HNT also increase. The results of materials characterization have shown that process of electrolysis proved successful in creating the metal-HNT nanocomposites [16].

4.2.8 Advantages of Using Electrolysis Technique for HNT Coating

It has many advantages of using the electrolysis technique for surface modification of HNT, and these include scalability potential, simple setup, and fabricating ability using nominal starting materials. Theoretically, it has been concluded that utilization of larger norm electrodes which are designed with a greater surface area can be utilized to synthesize the industrial level metal-HNTs scale amounts. This method of electrolysis for metal nanoparticle coating over HNTs is not limited to only Cu and Ag nanoparticles. This technique could be used to deposit other metals like palladium, gold, and platinum, and these metals show similar electrochemical behaviour during their deposition over HNTs during electrolysis.

5 Clay Nanotube Composite Antimicrobial Applications

5.1 Biomedical Applications of Halloysite Nanotubes

Biocompatibility is the most valuable attribute of halloysite clay nanotube-based composites which have some huge potential applications including wound healing medical implants, biosensors, nanomedicine, tissue engineering, and some drug delivery, etc. In further research, HNTs have lacking toxicity levels from low quantity. The comparative analysis of the recent research showed that (MWCNs) multi-walled carbon nanotubes, cytotoxicity of halloysite against blood vessels of mice assays (in vivo), and vein of human umbilical (in vitro) endothelial cells were. As the result, halloysite is more biocompatible to blood vessels than carbon nanotubes or multi-walled. HNTs have applications in anticancer therapy in the field of biomedical studies. Coating of halloysite nanotube enhanced the micro-scale flow device. The flow device of micro-scale can capture the (CTCs) circulating tumour cells from the blood of the patient [31].

The consumption or efficiency of the halloysite nanotube enhanced its (micro-tube) performance in killing and capturing cancer cells. Therefore, in this study, HNT loaded doxorubicin with magnetic particles and folic acid into (HeLa) cervical adenocarcinoma cells. Doxorubicin which is used is very toxic. The halloysite clay nanotube treats cancer cells by release of targeted anticancer agents. Anticancer agents are potential bioactive material that was used. In HNT, intercalation of anti-metabolite 5-fluorouracil developed the system of drug control release. For the treatment of cancer, it helps to remove drawbacks like quick metabolism, low absorption, and shortened half-life of 5-FU. Contrast ultrasound agents are used for exceptional delivery systems and echo graphic clinical imaging which includes wound care and patches of transdermal.

In biomedical applications, HNTs are used in the nonstop release of drugs, antiseptics, enzymes, and proteins. Nano-carriers in HNTs are called nano-bazookas. Continuously, nano-bazookas have therapeutic agents in which nano-bullets target

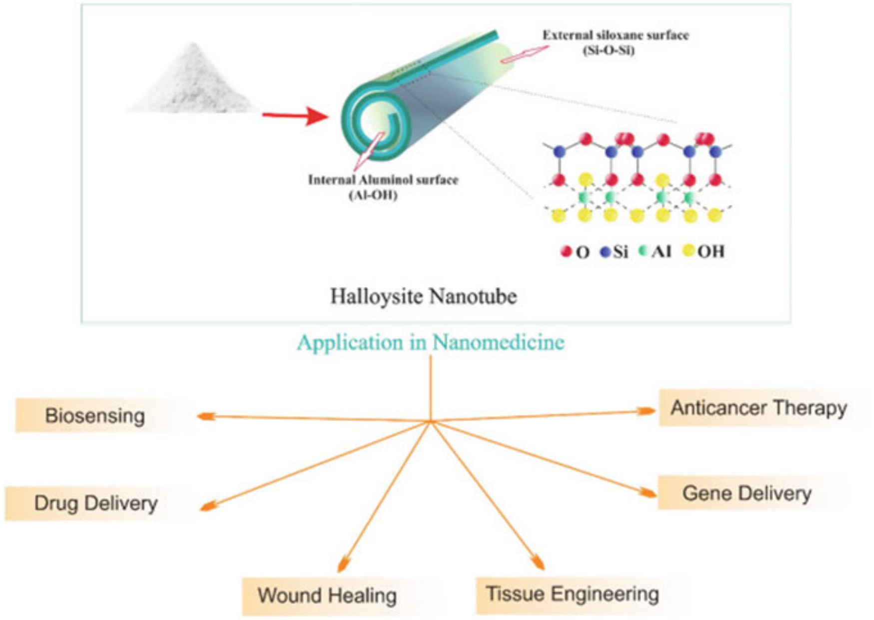


Fig. 2 Biomedical applications of clay nanotube-based composites (reproduced with permission under license no. 5443500511022 from the source [2, 34])

cancer cells. HNTs are readily available and used for systemic administration (intravenously). They have enhanced thermal and mechanical properties, and good biocompatible, as well as non-biodegradable. Potential material is formed by HNTs' non-biodegradability for the formation of nano-medicines, formulation of nanocomposites, implant developments, treatments of animals, etc. The HNTs can interrelate with polymers by the formation of polymeric composites through (H-bonding) hydrogen bonding, van der Waal, and electrostatic interactions. These relations of composite interactions are useful for their enhanced properties and the development of dispersed uniform composites [9] (Fig. 2).

5.2 *Liquids and Surfaces Protection and Disinfection by Clay Nanotubes-Based Composites*

There are an increasing number of infections that are acquired from the hospital. In health facilities, this type of infection is a very big issue. According to World Health Organization (WHO), the common way of transmission is by the indirect interaction in infectious diseases is transmitted with surface contaminants. These diseases are transmitted by sneezing, coughing, and talking of patients which produce infectious droplets. On surface contaminants, many different viruses and microbes can survive many days. The subsequent microbes are transferred to mucosal membranes of the nose, eyes, and mouth. Some reported infections and gastroenteritis outbreaks are spread by infected surfaces by hand contact. With the addition of microbial resistance, the effectiveness of antimicrobial agents is threatened seriously. World health organization WHO led a call for worldwide action in the 2016 General Assembly of the United Nations giving a political statement for antimicrobial resistance. Antibiotic resistance rate increases in highly developed nations among bacteria [39].

In Europe and the US, especially standard methods are used to stop long-time disinfection which includes disinfection solutions and wiping surfaces. Development with supportive antiseptic delivery could be economical and effective like aqueous chlorine dioxide spray. It has been reported that a definite quantity of durable antimicrobial schemes includes biocidal nanomaterials like light-activated photocatalysts and silver nanoparticles. These light-activated particles depend on phosphonium salts, TiO_2, and bactericide's surface-tethered quaternary ammonium compound. These nanomaterials are very effective against a broad array of microorganisms. HNTs halloysite clay nanotube formed with nanoparticles, loaded with medicine or drugs, and combined with paints to form the compound, or integrated into the hydrophobic surface. Zeta potential halloysites do not accept long stable aqueous dispersions when it is ca. -30 mV while the increases of HNTs zeta potential to -50–60 mV are by loading forcefully with anionic drugs in internal nanotube. Stable dispersions (water-based) are formed which are easily applied on surfaces relevant for favourable antibacterial sprays. For the purification of water, it has been seen that photocatalysts are used for the degradation of bacteria in a state photo-induced. Halloysite clay nanotubes HNTs act as a stabilizer which was used to support photo-catalytic nanoparticles to prevent the accumulation of nanoparticles. TiO_2 is a commonly used photocatalysts and has some of its nanocomposites [7].

For photo-catalytic disinfection, TiO_2 absorbs only wavelengths near to $\lambda <$ 400 nm UV region; it is almost 3% solar spectrum while it cannot utilize visual light with efficiency, and it has almost 43% of the solar spectrum. The modification in the bandgap is much expeditious visible light. A photo-catalytic method based on HNTs and TiO_2 were mainly tested for the degradation of waste product. It can also be used for antimicrobial applications. In UV-light antibacterial ZnO nanoparticles act as the photocatalyst. Absorbed ZnO nanoparticles in HNTs are formulated as a UV barrier for the formation of bacteria on membranes.

The bioactive properties of decorated halloysite nanotubes is by the function of silver nanoparticles for plasmonic inflammation. The measurement of optical absorption discovered wide plasmonic resonance for HNTs with silver nanoparticles in the part of 400–600 nm. The advanced samples were more noticeable under illumination which displays a bactericidal effect. Functionalized Ag-clay seems for antibacterial treatments of surfaces and liquids. These are stimulated by exposure to visible light. Due to plasmonic effects, gold nanoparticles could be applied in the same way. Gold coating halloysite-based HNTs core-shell construction showed the interconnectivity, thickness, and morphology of the Au. It may specify the photo-thermal capacity and optical response of plasmonic materials [9].

5.3 Tissue and Bone Engineering

In the recently developed research, halloysite clay which contains antibacterial particles has various functional groups used in many types of medical applications, polymeric films, and coatings. An electrospinning technique used to make nanofibres has been widely considered for different applications and tissue engineering. Due to the polymers used, drug-loaded fibres are biocompatible while due to polymer degradation they have antibacterial properties by the release of the drug slowly. Poly (lactic-co-glycolic acid), polylactic acid, poly (caprolactone) or gelatin, and polycaprolactone are used for making various fibres composites of halloysite polymer in the studied for antimicrobial protection. Lacticoglycolic acid (electrospun poly) nanofibres were changed with HNTs to form a system of drug delivery with a slow release of tetracycline hydrochloride. The drug loading efficiency was 42.65%. The inclusion of positively charged tetracycline hydrochloride into the electrospinning solution by halloysite loading shows a lower fibre diameter [41].

The halloysite nanofibrous mats exhibit useful antibacterial activity, revealed good cytocompatibility, and in both solid and liquid mediums, it can show bacterial growth. Drug-loaded halloysite with free percentages nanofibrous mats in 42 days in low quantity than the first day which contains tetracycline hydrochloride and pure drug with nanofibres. In electrospinning drug-loaded halloysite clay nanotubes, due to constant drug delivery bone regeneration membranes were developed. Clay nanotubes doped into polycaprolactone or gelatin microfibres. Halloysite nanocontainers are used for advanced research in a clinical study by attaining new dental types of equipment with some properties of antimicrobial and bioactive in our daily life. As a delivery system of the drug, HNTs nanotubes play an important role in the establishment of dental coatings [26].

By using different types of alcoholic suspensions, the coatings of chitosan composite were deposited electrophoretically (EPD). Composites of chitosan coatings are also known as vancomycin-loaded halloysite nanocomposites. Suspensions of ethanol were selected by increasing the electrophoretically (EPD) rate as the best possible method, and the coatings are formed with comparatively high violence and with high absorbent content or non-absorbed chitosan. Drug-loaded coating against S.aureus showed almost 27% (higher) antibacterial activity as compared to without loaded drugs with a similar coating [39].

5.4 Antimicrobial Applications of Zinc Oxide Nanoparticle

The excellent properties of zinc oxide (ZnO) have attracted by its great interest worldwide. The understanding of the development of nanoparticles has shown particular results. An appreciable survey of ZnO-NPs has been activated by using various types of synthesis methods for the production of nanomaterials and its upcoming applications, high luminescent ratio allowed with the increasing number of excitation

Table 1 Applications of Zn nanoparticles [2]

Applications of Zn or ZnO particles		
Sr. no.	Application's fields	Examples
1	Electronics and energy	Nanogenerator power sensors based on ZnO nanowires, low-cost solar cells
2	Cosmetic's industry	Minerals cosmetics, UV filters in sunscreen, antimicrobial food packaging
3	Medicine and biology	Drug and gene delivery, bioimaging
4	Materials and manufacturing	Chemical sensors based on ZnO, antimicrobial textiles, protections from exposure to UV rays

binding energy like 60 meV while the wide bandgap is almost 3.36 eV. In the packaging of food area (UV), ultra-violet protective agents are used while ZnO-NPs are commonly used as an antimicrobial. ZnO-NPs drive the synthesis methods of nanomaterials by increasing the focus on advanced improvement for its applications and functions (Table 1).

5.5 *Wound Dressing*

Halloysite nanotubes is used for the manufacture of multi-layer flexible wound dressings which contains many different functions like tissue regeneration, fluid absorption, fungal protection, and antibacterial protection. The dressing might be used as a pad or topical gauze, or as packing of wound material for both therapeutic and prophylactic interventions. Clay-nanotube HNTs are used for advanced properties of dressing, to load numerous drug sets possibilities, or increased dominance over the release kinetics drugs. All these are encouraging properties to deal with multiple infections of microorganisms, to heal chronic wounds, and also used for behaviour of multi-vector [34].

The antiseptic elastic nanocomposite combined with dual drug co deliveries was formed by sulphate-loaded HNTs clay nanotube composites polymyxin B and ciprofloxacin into the gelatin elastomer. Polymyxin B sulphate was dispersed in the matrix by loading halloysite nanotube while the ciprofloxacin nanoparticles were distributed directly into the matrix. Ciprofloxacin nanocomposites are those particles that proceed against both gram-negative and gram-positive bacteria. Both polymyxin loaded HNTs halloysite and ciprofloxacin were affected by the formulation of some basic physical characteristics like fibroblast adhesion, in vitro drug release, proliferation, and cytotoxicity [13]. The properties of antibacterial were also investigated by the effect of these loaded halloysites. Drug-loaded halloysite showed the rate of dissoluble high polymyxin B sulphate which were liberated, and it also improved the strength of matrix tensile [35] (Fig. 3).

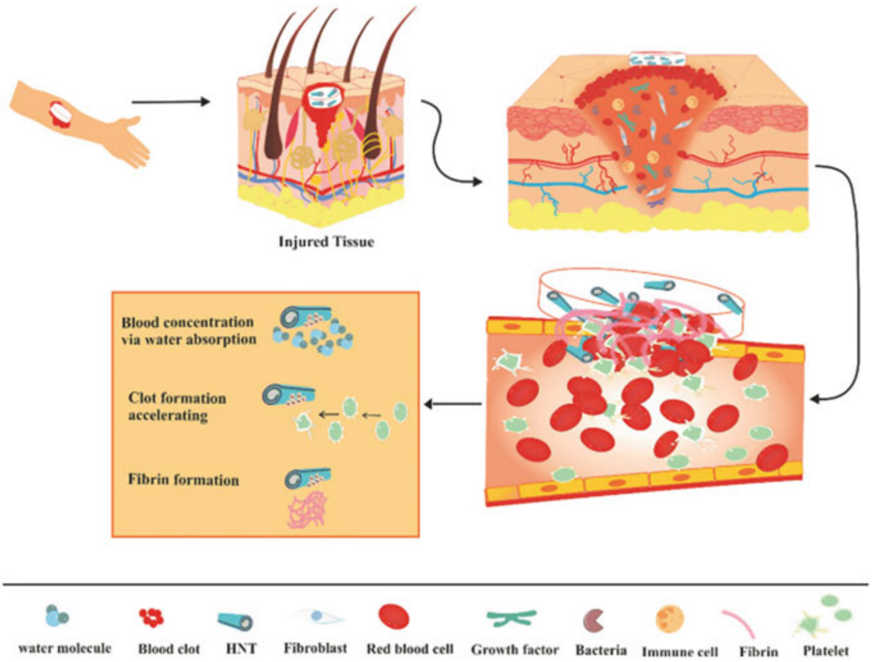


Fig. 3 HNTs nanocomposites schematic illustration of wound dressing (reproduced with permission under license no. 5446481059102 from the source [2, 34])

5.6 Filtration Membranes with Enhanced Antibacterial Activity

In this report, halloysite clay nanoparticles doped ultrafiltration membranes. These filtration membranes work with organic content in water. The high content of organic compounds increases consumption energy and decreases the lifetime of membranes by inhabiting biofouling. The composition of antibacterial agents with functionalized nanotube composites helps to control the evolution of biofilms. The membrane is formed by the use of a halloysite nanotube which allows for preventing bio-contaminants and for the antimicrobial properties [39].

(a) The synthesized halloysite clay nanocomposites (calamine) were added almost 1–3 wt% to the filter membrane (polyethersulfone).
(b) The hybrid membranes have a lower rough surface than the membrane of pure polyethersulfone by thermos-mechanically stable membrane. It also had been increased the water flux. With the addition of HNTs halloysite, the membrane has enhanced hydrophilicity.
(c) Clay nanotubes have preservative enzymes that act as antibacterial agents naturally. This creates another biofilms problem.

(d) Hallosyites brought to functionalization by lysozymes which has been covalently grafted with carboxylic groups. It was used to prepare ultra-filtration membranes of hybrid antibacterial by adding lysozyme into polyethersulfone.

(e) The antibacterial test shows that hybrid HNTs membranes indicated the good performance of antibacterial. It was also used to treat wastewater.

(f) Ultrafiltration polyethersulfone membranes produce qualified loaded halloysite which contains A nanoparticles. By phase invention, copper ions were processed.

(g) In an early study, Ag nanoparticles were grafted. Chemical modification of silane with halloysite is used for the formation of Cu^{2+} halloysite and the complexing of Cu-ions by mixing copper dichloride.

(h) Tests of hybrid membranes showed good antibacterial properties. Good antibacterial properties have more than 99% protective rates against S. aureus and E. coli nanomaterials.

5.7 Food Contact Materials

Materials of food packages that have polymeric films are susceptible to biofilm formation and bacteria colonization. Fruits, fish, bread, meat, cheese, and vegetables are particularly highly sensitive to fungi and bacteria. Polymer composites are developed with fillers of antibacterial which prevent food from decomposition and another important fact is the growth of microorganisms. In the food packaging industry due to biodegradability and minimal environmental effect, different variety of antimicrobial agents have been tested which contains plant extracts, natural polymers, and essential oils. Essential oils are very important and have well-known activity levels which are traced from plants. Due to essential oil volatility, it is difficult to integrate polymers [37].

Halloysite nanotubes HNTs in the recent research were used as active sites of carriers. During the high-temperature essential oil contains protective high antimicrobial properties and combinations of polymers in a specific time [19]. Halloysite or carvacrol has a continuous antimicrobial activity and has less density than used polyethylene films. These antimicrobial properties showed against L. innocua and E. coli, and they also showed fungicidal action. Halloysite nanotubes HNTs showed synergistic antibacterial properties when mixed with thymol and carvacrol. Rosemary oil with a hybrid of pectin-halloysite-based nanocomposites has great potential for packaging. Thyme oil-loaded HNTs halloysite used in paper packaging process showing the powerful antibacterial property for 10 days processing against E. coli. By using many different processes halloysite nanotubes are loaded with organic antibacterial molecules. The natural process of kinetics from inorganic and organic hybrids of respective agents and clay nanotube-based composites are presented [21] (Fig. 4).

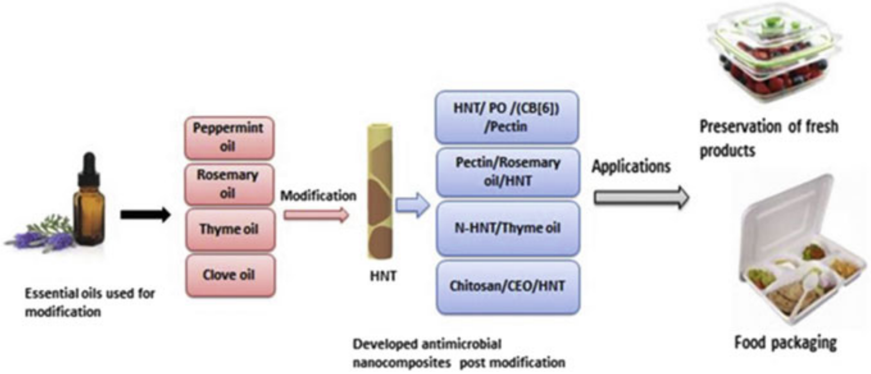


Fig. 4 Antimicrobial HNTs nanocomposites for food contact materials (reproduced with permission under license no. 5446490446773 from the source, [2, 33])

5.8 Dentistry

Dentistry is the science of studying which has two main terms oral medicine and dental medicine which are used to explain the conditions of the oral cavity, diagnosing, prevention of oral diseases, supporting structures and treatment, disorders, and particularly dentition. On the other hand, dentistry has (jaw and facial) maxilla facial region which contains oral mucosa, related and adjacent tissues, and structures. Dentistry study is not only related to teeth and gum diseases, and it also has some other diagnoses in the temporomandibular joint and supporting like nervous, anatomical structures, vascular, muscular, and lymphatic structures. HNTs nanocomposites are generally used in implants, resins, composites, and cement. Halloysite clay nanotubes HNTs make a potential target in dentistry material which includes antibacterial activities, non-toxicity, high mechanical strength, and biocompatibility [3].

In the root canal treatment dead pulp and infected tissues were removed. This treatment is also known as endodontic therapy. Primary infections resist the process of antimicrobial which is associated with intercanal and its pathogens. Therefore, in the process of filling, the root canal microbes targeted secondary infections [20]. In various researches, the modification of polymeric resins has been studied which contains halloysite nanotube HNTs. By improving antibacterial activities, it is observed that the mechanical behaviour is enhanced which contains breaking energy, modulus, and flexural strength. In another related study, the Farnesol-loaded halloysite HNTs are used as fillers to analyse their mechanical and physicochemical properties. The addition of Farnesol-HNTs mass fraction increases the conversion degree, compression strength, and flexural strength. According to this study, Streptococcus mutants have increased the zone of inhibitions and also have increased biocompatibility against the fibroblast cells of mouse embryonic which are called NIH-3T3 cell lines [31].

Scientists also configured silver mobilized halloysite which has better mechanical behaviour, and biological and physicochemical activities to examine dental problems, in which composite materials do not show fundamental cytotoxicity against the cell lines of NIH-3T3. In dentistry, dental resins are prepared with or without conventional glass fillers which are named TEGDMA or Bis-GMA. There is no significant increase in mechanical activity which was observed by increasing properties after having an increased (5%) amount of fraction. Dental resin TEGDMA or Bis-GMA have composites of substantial mechanical. HNTs clay nanotubes are used to deliver drug material to diseases affected in the field of dentistry. This technique reduces the side effects of related dosage by depositing a selected controlled quantity of drugs. It is beneficial to release the controlled decay of drugs at right time [39].

Minocycline microspheres (MM) are also known as Arestin. It delivers continuously releasing of minocycline MM to the periodontium. Ceramic bridges and crowns meet functional and aesthetic demands like alumina or zirconia. They have low elasticity with a brittle structure. Halloysite nanotubes gelatin-modified (HNTs-g) are used as an advanced nano-fillers system (ATH-sil) which has aluminium trihydrate with silane-coupling. Synergistically observed the methyl methacrylate monomer and methyl methacrylate (mMM/ MM) which affect acrylic materials. They analyse different studies like abrasion resistance, hardness, and solution of buffer absorption. In any case of examining dental applications, they performed fall tests [34].

6 Conclusions

To conclude, clay nanotube is included in one of the emerging trends in nanotechnology because of its unique biocompatibility and excellent antimicrobial properties. These are double-layered spherical or tubular in a structure containing clay silicate with thin plates. Originally, HNT formed from volcanic deposits containing glass and volcanic ash. The structural composition of HNTs is in such a way that on the surface of clay nanotube, hydrogen bonding formation in the aluminium and siloxane groups with biomolecules. Clay nanotubes are natural sources that provide biomedical applications because they are very cheap, biocompatible, cytocompatibility, and nontoxic materials.

The HNTs polymer composite contains halloysite, hectorite, bentonite, and montmorillonite. Functional groups of clay nanotubes also called nanocontainers to have different pH ranges such as 8.5pH with positively charged in tubule inner lumen and 1.5 pH with a negative charge. The surface charges of HNT include internal (Al-OH) and external (Si-O-Si) surfaces. Clay nanotubes used polymeric films and fibres for filling composite materials which allow bacterial protection in the study of SiO_2-surface chemistry. HNTs are used for the formulation of fabric coatings, wound dressings, dental materials, and fibres for tissue engineering.

Formulation of antibacterial HNTs is being tested in research lab, and they are medically utilized but still need more qualified clinical studies. These halloysite clay nanotubes are also good for drug delivery systems when a topical effect is needed. In different biomedical applications, clay minerals have well-defined properties which include surface area, porosity, pore size, biomechanical properties, and physicochemical. The continuous release of therapeutic agents can be remarkably increased in an aqueous environment. With specific chemistry of halloysite, superior loading rates, and high surface area, the hybrid materials could provide for biomedical applications in tissue engineering, and dentistry to facilitate someone in enlarging the potential use of polymeric nanotube-based composites.

References

1. Abdullayev, E.S.: Natural tubule clay template synthesis of silver nanorods for antibacterial composite coating. ACS Appl. Mater. Interfaces **3**(10), 4040–4046 (2011)
2. Baranwal, A.S.: Prospects of nanostructure materials and their composites as antimicrobial agents. Front. Microbiol. **9**, 422 (2018)
3. Barot, T.R.: Physicochemical and biological assessment of silver nanoparticles immobilized Halloysite nanotubes-based resin composite for dental applications. Heliyon **6**(3), e03601 (2020)
4. Bhattarai, R.S.: Comparison of electrospun and solvent cast polylactic acid (PLA)/poly (vinyl alcohol)(PVA) inserts as potential ocular drug delivery vehicles. Mater. Sci. Eng., C **77**, 895–903 (2017)
5. Boyer, C.J.: Clay Nanotube Composites for Antibacterial Nanostructured Coatings. Louisiana Tech University (2016)
6. Bustamante-Torres, M.A.-V.-N.-V.: Antimicrobial activity of composites-based on biopolymers. Macromol **2**(3), 258–283 (2022)
7. Cavallaro, G.L.: Halloysite nanotubes for cleaning, consolidation and protection. Chem. Rec. **18**(7–8), 940–949 (2018)
8. Choudhury, M.B.: Antimicrobial polymeric composites in consumer goods and healthcare sector: a healthier way to prevent infection. Polym. Adv. Technol. **33**(7), 1997–2024 (2022)
9. Danyliuk, N.T.: Halloysite nanotubes and halloysite-based composites for environmental and biomedical applications. J. Mol. Liq. **309**, 113077 (2020)
10. Fakhruddin, K.R.: Halloysite nanotubes and halloysite-based composites for biomedical applications. Arab. J. Chem. **14**(9), 103294 (2021)
11. Fatima, N.Q.: Recent developments for antimicrobial applications of graphene-based polymeric composites: a review. J. Ind. Eng. Chem. **100**, 40–58 (2021)
12. Ganguly, P.B.: Antimicrobial activity of photocatalysts: fundamentals, mechanisms, kinetics and recent advances. Appl. Catal. B **225**, 51–75 (2018)
13. Gaskell, E.E.: Antimicrobial clay-based materials for wound care. Fut. Med. Chem. **6**(6), 641–655 (2014)
14. Gomes, M.G.-S.: Optimizing CNT loading in antimicrobial composites for urinary tract application. Appl. Sci. **11**(9), 4038 (2021)
15. Gorrasi, G.: Dispersion of halloysite loaded with natural antimicrobials into pectins: characterization and controlled release analysis. Carbohyd. Polym. **127**, 47–53 (2015)
16. Jee, S.-C.M.-S.: Assembling ZnO and Fe_3O_4 nanostructures on halloysite nanotubes for antibacterial assessments. Appl. Surf. Sci. **509**, 145358 (2020)
17. Kamarudin, S.H.: A review on antimicrobial packaging from biodegradable polymer composites. Polymers **14**(1), 174 (2022)
18. Kim, T.K.: Preparation of melt-blending polylactic acid/halloysite nanotube composite films for improvement of tearing strength. Text. Sci. Eng. **57**(3), 192–197 (2020)
19. Lagaron, J.M.: Improving packaged food quality and safety. Part 2: Nanocomposites. Food Addit. Contamin. **22**(10), 994–998 (2005)

20. Lam, S.M.: MXenes and their composites for potential antimicrobial applications. In: Mxenes and their Composites, pp. 525–551 (2022)
21. Li, Q.R.: Applications of halloysite nanotubes in food packaging for improving film performance and food preservation. Food Control **124**, 107876 (2021)
22. Liu, M.B.: Antimicrobial polymeric composites for high-touch surfaces in healthcare applications. Current Opinion in Biomedical Engineering, p. 100395 (2022)
23. Lvov, Y.: Functional polymer–clay nanotube composites with sustained release of chemical agents. Prog. Polym. Sci. **38**(10–11), 1690–1719 (2013)
24. Lvov, Y.M.: The application of halloysite tubule nanoclay in drug delivery. Expert Opin. Drug Deliv. **13**(7), 977–986 (2016)
25. Maruthapandi, M.S.: Antimicrobial activities of conducting polymers and their composites. Macromol **2**(1), 78–99 (2022)
26. Naumenko, E.: Halloysite nanoclay/biopolymers composite materials in tissue engineering. Biotechnol. J. **14**(12), 1900055 (2019)
27. Ogunsona, E.O.: Engineered nanomaterials for antimicrobial applications: a review. Appl. Mater. Today **18**, 100473 (2020)
28. Omerović, N.D.: Antimicrobial nanoparticles and biodegradable polymer composites for active food packaging applications. Compreh. Rev. Food Sci. Food Saf. **20**(3), 2428–2454 (2021)
29. Palza, H.: Antimicrobial polymers with metal nanoparticles. Int. J. Mol. Sci. **16**(1), 2099–2116 (2015)
30. Paul, D.R.: Polymer nanotechnology: nanocomposites. Polymer **49**(15), 3187–3204 (2008)
31. Peña-Parás, L.S.-F.: Nanoclays for biomedical applications. Handbook of ecomaterials **5**, 3453–3471 (2018)
32. Pettinari, C.P.: Antimicrobial MOFs. Coord. Chem. Rev. **446**, 214121 (2021)
33. Saadat, S., Pandey, G., Tharmavaram, M., Braganza, V., Rawtani, D.: Nano-interfacial decoration of Halloysite Nanotubes for the development of antimicrobial nanocomposites. Adv. Colloid Interface Sci. **275**, 102063 (2020)
34. Same, S.N.: Halloysite clay nanotube in regenerative medicine for tissue and wound healing. Cerami. Int. (2022)
35. Sandri, G.A.: Halloysite and chitosan oligosaccharide nanocomposite for wound healing. Acta Biomater. **57**, 216–224 (2017)
36. Santos, A.C.: Halloysite clay nanotubes for life sciences applications: from drug encapsulation to bioscaffold. Adv. Coll. Interface. Sci. **257**, 58–70 (2018)
37. Sarfraz, J.G.-S.-N.: Nanocomposites for food packaging applications: an overview. Nanomaterials **11**(1), 10 (2020)
38. Sharma, S.S.: Tailoring the mechanical and thermal properties of polylactic acid-based bionanocomposite films using halloysite nanotubes and polyethylene glycol by solvent casting process. J. Mater. Sci. **54**(12), 8971–8983 (2019)
39. Stavitskaya, A.B.: Antimicrobial applications of clay nanotube-based composites. Nanomaterials **9**(5), 708 (2019)
40. Sun, D.B.: Antimicrobial materials with medical applications. Mater. Technol. **30**(sup6), B90–B95 (2015)
41. Wong, L.W.: Natural hollow clay nanotubes and their applications as polymer nanocomposites in tissue engineering. J. Sci. Adv. Mater. Dev. 100431 (2022)
42. Xue, J.W.: Electrospinning and electrospun nanofibers: methods, materials, and applications. Chem. Rev. **119**(8), 5298–5415 (2019)

Clay-Based Nanocomposites and Hybrid Membrane for the Treatment of Wastewater

C. Arun, A. Sethupathy, and Rangabhashiyam Selvasembian

Abstract Rapid increase in industrial and different forms of commercial activity all over the globe generates large volume of wastewater. The major source of wastewater is from the industrial sectors such as petrochemical, food processing, refineries and metallurgical, mining, tanning, and electroplating, which are associated with unprocessed oil and heavy metals in larger proportions. The discharge of these types of wastewaters into the nearby water bodies causes harmful impacts on living organism. Recent year's sustainable uses of membrane in combination with different materials are getting attractions among researchers in the field of water treatment. Present chapter focuses on the clay-based hybrid membrane potentials in the removal of different types of wastewater pollutants and discusses the approaches involved in the clay-based hybrid membrane synthesis, characterization, and their application in the wastewater treatment. The nanocomposite precursors sourced from different clay minerals in membrane preparation are taken in account. Further, the future perspectives of the clay-based hybrid membrane to overcome the drawback in the field of membrane-based technology and toward the sustainable applications are also presented.

Keywords Clay · Nanocomposite · Hybrids · Membranes · Water pollutants · Treatment

---

C. Arun
Department of Biotechnology, Periyar Maniammal Institute of Science and Technology (Deemed to be University), Vallam, Thanjavur, Tamil Nadu 613403, India

A. Sethupathy
Department of Chemical Engineering, Anjalai Ammal Mahalingam Engineering College, kovilvenni, Thiruvarur, Tamil Nadu 614403, India

R. Selvasembian (✉)
Department of Environmental Science and Engineering, School of Engineering and Sciences, SRM University-AP, Amaravati, Andhra Pradesh 522240, India
e-mail: rambhashiyam@gmail.com

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_20

1 Introduction

In recent decades, decline of water resources increases the demand of water all over the globe. Siddeeg et al. [49] pointed out that the natural water resources are major polluted by the wastewater discharges from several industrial processes. Naidu et al. [46] reported that most of the natural water resources contain more than 700 carcinogenic and other organic and inorganic microcontaminants. Inorganic compounds like chromium, lead, arsenic, mercury, etc., and organic compounds like dye, pigments, and others phenolic compounds are difficult to degrade and to remove from wastewater. Due to increase of urban community and industrialization, the requirement of water increases, and it can be fulfilled by sustainable water treatment process, recycle and reuse of wastewater. Pre-treatment and treatment of wastewater are required to remove various organic, inorganic, and pathogens which are important for the supply of hygienic water for human activities, agricultural, and industrial activities [45]. Different types of wastewater treatment like membrane separation [21] and filtration (reverse osmosis, ultrafiltration, microfiltration) [19], precipitation [15], Electrocoagulation [50], Adsorption [13], Electrolysis [16], Electrocatalysis [4], most of them are associated with the negative factors of high cost, complex design, pollution generations, etc. The efficient treatment of wastewater becomes one of the essential factors for the economic growth in most of the developing nations. It is challenging to formulate and implement unconventional wastewater treatment methodology with greater efficiency lower capital cost and sustainable technology. In recent days, the use of nanomaterials, ceramic membranes formulation, and modified adsorption materials has increased among researchers over other conventional waste treatment process. Judd and Jefferson [28] stated that membranes are thin layer of selective barrier used in separation and purification process. A membrane technology like ultrafiltration, nanofiltration, microfiltration, and reverse osmosis commonly works according to the principle based on pressure difference or size difference between the feed materials and permeate comes out of the selective membrane. The membrane techniques are also working according to different driving forces like concentration gradients, chemical, electrochemical and thermal gradients [62]. Ang et al. [5] stated the membrane process can be done in two different ways: standalone (membrane process without additional treatment process) and hybrid systems (membrane process with additional treatment process). Drioli et al. [23] reported that in hybrid systems along with membrane process, other treatment technologies are involved to obtain a higher performance than standalone system through higher removal efficiency of waste and toxic materials from feed wastewater, lowering the fouling issue during the operations and also helps to obtain higher amount of treated water. On other hand, [51] and Chen and Caruso [17] reported that nanoparticles can be prepared by breaking down of larger particles to smaller particles, and the same can be used in different environmental remediation process effectively. Meyer and Upadhyayula [43] stated that number of nanomaterials with higher surface area helps to remove microbial species, organic and inorganic compounds from wastewater. But the production costs of the nanomaterials and ceramic membranes made it uneconomical to use in water and wastewater treatment process. To formulate effective and implement large unit of water and wastewater treatment using ceramic membrane technology, low cost, and eco-friendly raw materials like clay, ash, sands, etc., can be used. The present chapters discuss about the development in substantial material and eco-friendly process for the formulation of low-cost clay-based nanocomposites and hybrid ceramic membrane. This chapter discusses about various applications in water and wastewater treatment process and the challenges in forthcoming improvement of clay-based wastewater treatment process.

2 Clay Minerals

Clay minerals are widely called as hydrous aluminum phyllosilicate (Fig. 1), which have capacity to retain water and dissolved plant nutrients as they have unbalanced net negative electrical charge on their surface area. Because of that properties, clay minerals have excessive adsorption capability of contaminants in wastewater [8]. Natural clay minerals can be used to remove organic and inorganic contaminants in wastewater, but effectiveness of treatment is not effective when compared to chemical processing of wastewater treatment because of their less surface area and lack of knowledge on reuse and recovery of natural clay material from aqueous system [57]. Some of the researcher working to increase the surface area, by preparing nanoclay materials from different class of clay minerals like kaolin, kaolinite, montmorillonite, bentonite, illite, and micas [8]. Unuabonah and Taubert [55] state polymer resin has the properties to overcome the downsides of natural clay minerals, but the resin is depended on pH for its effective removal of contaminants. Polymer resin is also too expensive and has poor water holding, etc. Recent days in order to overcome the disadvantages of clay and polymer resin in removal of pollutants from water, some of the researchers develops a nanocomposite made up of clay and polymer to attain a sustainable material.

2.1 Clay Polymer Nanocomposites (CPN)

LeBaron et al. [34] stated that clay polymer nanocomposites have beneficial characteristics of natural clay like eco-friendly, available enormously, cheaper in cost large, and also has the properties of poly-resins like higher adsorption efficiency, higher surface area, and proper regeneration. It can be formulated in micro or nano-size in a sustainable way, and it can be also being employed in removal of various contaminants from wastewater effectively [53, 12]. Different types of clay polymer composites are formulated using polymers like chitosan, polystyrene, poly vinyl chloride epoxies, polyurethanes, polypropylene, and polyesters. Some of the clay

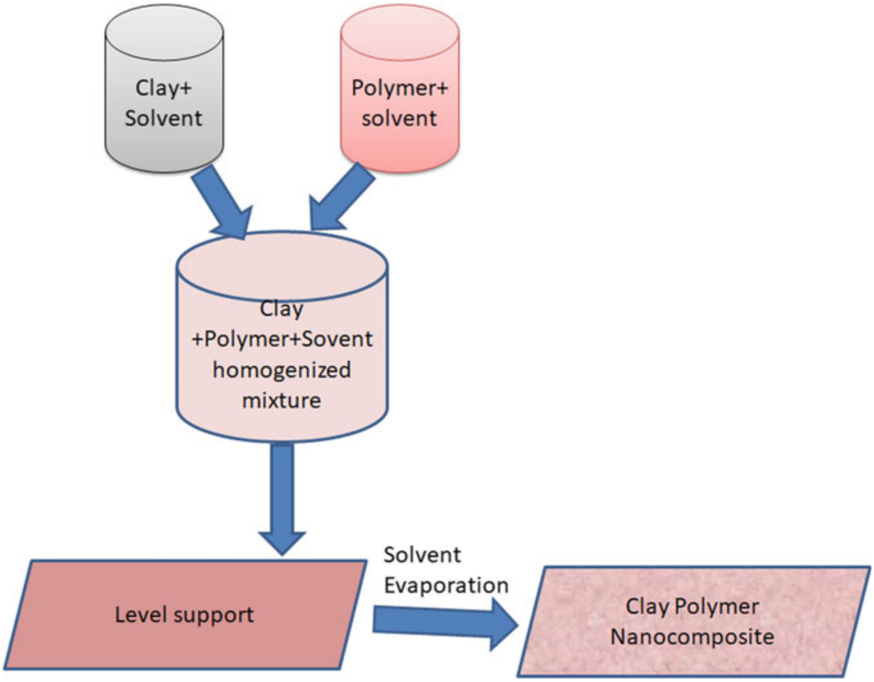


Fig. 1 Solution-blending technique—clay polymer nanocomposite formulation

polymer composites commonly used in wastewater treatments are polyurethane–clay nanocomposites, epoxy–clay nanocomposites, clay–biopolymer nanocomposites [33], polyimide–clay hybrid [59], organoclay–polymer blend, polystyrene–clay nanocomposite, polysiloxane–clay nanocomposite, magnetic clay–polymer nanocomposites [39].

2.1.1 Preparation of Clay–Polymer Nanocomposites

Clay–polymer nanocomposites are prepared using following three common methods.

Solution-Blending Technique

In this method, solvent was mixed with polymer and clay separated in two different containers then solution made of clay and solvent pour on to polymer solvent mixture and kept for a period of time to become homogenized (Fig. 1). Then, the whole homogenized clay–polymer–solvent mixture added to level support (film or glass plate used for membrane formulation) and then using evaporation process solvent will be removed from the mixture to form a clay polymer composites [2, 3]. Gurses

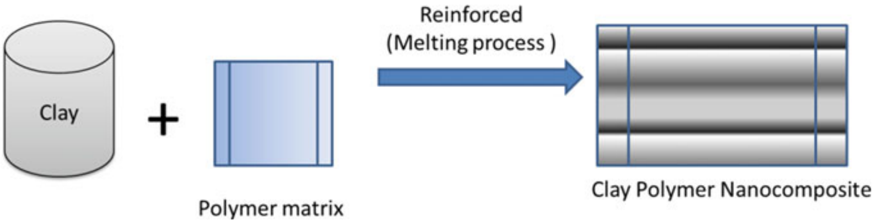


Fig. 2 Melt bending method—clay polymer nanocomposite formulation

[25] stated that solution blending process contains three major steps namely the clay dispersion in polymer solution, removal of solvent, and composite film formation. Arya et al. [7] synthesized magnetic polymer/nanoclay composites by solution blending method using chitosan, powdered activated carbon, and magnetic nanoparticles in optimal ratio of 1:0.5:0.3:0.3, respectively. To increase the stability and polymer clay nanocomposite yield, reduce clay dispersion time, and reaction time between polymer and clay, ultrasonication process can be used in place of mechanical agitator for blending [47].

1. Melt Bending Method

In this methodology, the clay minerals are reinforced onto the polymer matrix using melt integration methodology. Guo et al. [24] stated that melting temperature used in this method will be greater than melting temperature of polymer as result stable strength clay polymer nanocomposites can be formulated (Fig. 2).

Melt bending method can be processed either in static mode or dynamic mode. When it operates in static mode, then it should carry out under vacuum with temperature above 50 °C [42]. Moustafa et al. [44] synthesized a biodegradable polymer/nanoclay composite using a natureplast PBE 003/poly (butylene adipate-co-terephthalate) by melt blending method, and the resulted clay nanocomposite has optimal tensile strength at 5% organoclay, and it has the property of water vapor permeability barrier.

2. In Situ Polymerization Technique

In this methodology, the clay monomer was polymerized on to the polymer matrix (Fig. 3). The results from compression casting made the clay polymer nanocomposites become more strengthen and have a uniform dispersion of clay on to polymer matrix [1].

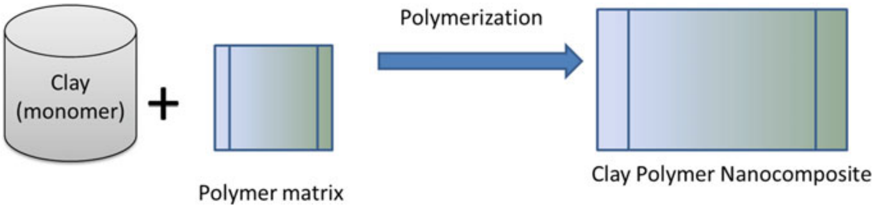


Fig. 3 In situ polymerization method—clay polymer nanocomposite formulation

3 Formulation of Iron Oxide–Clay Nanocomposites

Tokarcíková et al. [52] reported that the co-precipitation of clay minerals with magnetic iron oxide in the alkaline environment using NaOH results in iron oxide–clay nanocomposites (Fig. 4). To improve the strength of iron oxide–clay nanocomposites, heating using microwave and reflux system [31] can be incorporated. Belachew and Bekele [11] stated that the combination of oxidation and co-precipitation methods helps to produce homogenized iron oxide–clay nanocomposites.

In situ polymerization method for formulation poly(glycidyl methacrylate)/MMT composites along with ultrasonication process gives improved reaction and product nanocomposite yield when compared to solution blending with ultrasonication process [18]. Zang et al. [61] prepared a composite using silver and attapulgite clay using in situ polymerization method shows higher ant bacterial activity due to proper formation of clay fillers in polymer matrix.

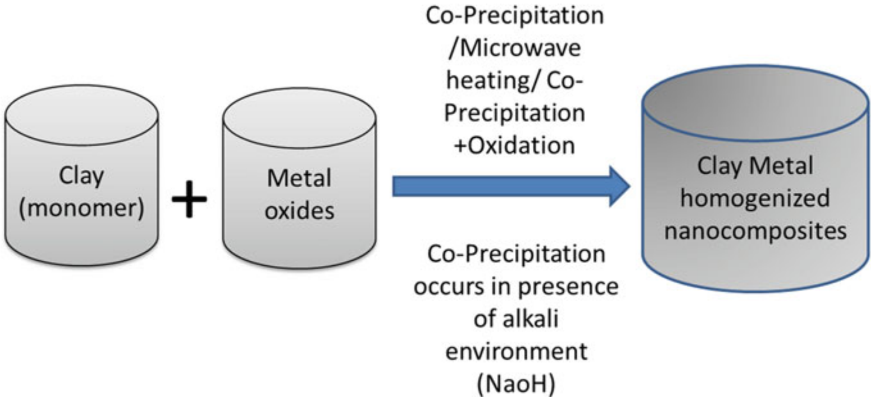


Fig. 4 Formulation of iron oxide–clay nanocomposites

4 Formulation of Clay Nanocomposites Membrane

The membrane-based clay nanocomposites formulation was done in four major steps batching, milling (crushing), sieving and mixing (Fig. 5). The selection of inorganic powder is significant to produce a membrane with desired particle shape, particle size, and particle distribution which in turn affect the pore size, pore size distribution, and porosity of final membrane produced. Hubadillah et al. [27] reported kaolin and expanded polystyrene for the production of hybrid membrane. Different hybrid membranes were produced using different ratio of polystyrene 0–20% and found maximum dye removal found using hybrid membrane made of 20% polystyrene and 80% kaolin adsorbed optimal methylene blue from water.

Jung-Hye et al. [29] formulated clay-based membrane to remove oil from oily wastewater from the mixture of kaolin, bentonite, talc, sodium borate, and carbon black and consequent heated at 1000 °C. The result shows increase in oil rejection according to pressure applied and amount of carbon black.

Hubadillah et al. [27] reported studies on kaolin-based low-cost membranes are used mainly to remove pathogen and oil from wastewater. Kaolin-based low-cost membranes have many advantages over ceramic oxides as it can be fabricated at lower temperature and also it works with and without additives processing. The mechanical strength of kaolin-based membranes is mainly depended on pore size, porosity and mineralogy, which can be identified using additives and sintering temperature used for the formulation. Membrane formulation using attapulgite or palygorskite clay also plays vital role in wastewater treatment process. Zhu and Chen [62] stated that attapulgite-based membrane not requires higher temperature for formulation, and it has pore size around 12 nm, and porosity is more than 60% which is higher when compare to conventional ultra-filtration membrane.

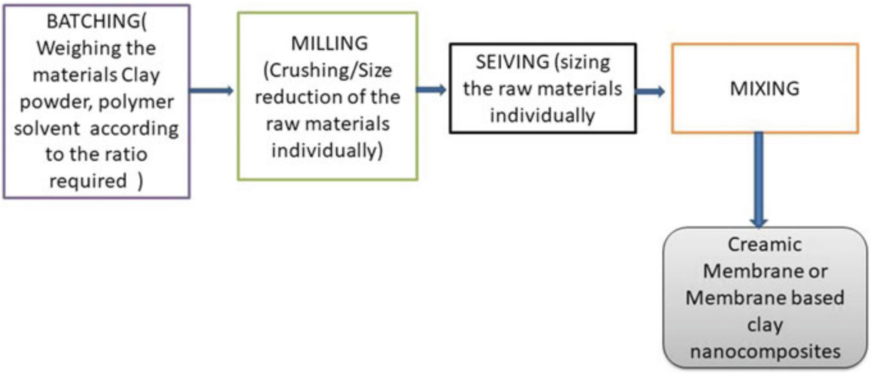


Fig. 5 Steps involved in membrane-based clay nanocomposites formulation

4.1 Application of Clay Membrane Nanocomposites in Wastewater Treatment

Removal of Dye

Mukhopadhyay et al. [45] stated that polymer membrane clay nanocomposites are commonly used in purification of water and removal of contaminants form wastewater because of it properties low formulation cost, flexibility in treatment process, and stability of nanocomposites. Ahmed and Sayed [32] used the kaolin and polystyrene for the formulation of polymer membrane clay nanocomposites (Hybrid membranes) to remove methylene blue dye from water. The study relieved that hybrid membranes formulated with 20% of polystyrene by weight shows higher removal of methylene blue as it helps to increasing pore volume and also helps to decreasing the bulk density. Ahmad et al. [3] stated that bentonite PVC hybrid membrane shows higher % of oil removal with 18 g of PVC loading for membrane preparation. Daraei et al. [20] formulated microfiltration membranes using poly (vinylidene fluoride) helps to remove dyes from wastewater. Table 1 shows some of the studies used nanocomposites for dye removal and their adsorption capacity.

The clay nanocomposites membranes needed more improvements in sustainable formulation using cost-effective raw materials that help to remove dye components from wastewater in developing countries also.

Table 1 Nanocomposites for dye removal

Dye	Nanocomposite	Adsorption capacity (mg/g)	References
Malachite green	Amine-modified polyacrylamide–bentonite nanocomposite	656.5	[6]
Methylene blue	CTS-g-poly(acrylic acid)/Montmorillonite clay (MMT) nanocomposite	1859/322	[58]/[41]
Crystal violet	sepiolite nanocomposite hydrogels	47	[57]
Azo dye	CTS/bentonite	323	[37]
Safranine-T and brilliant cresyl blue	Acrylamide (AAm)-2-acrylamide-2-methylpropanesulfonic acid/clay hydrogel nanocomposite	495	
Brilliant green and acid red 1	adsorbent-based composite coating (mixture of bentonite, acrylic polymer, and polyethylene-diamine)	255	[9]

4.2 Removal of Microbial Contaminants

Pathogenic microbes (*Salmonella typhi*, *Shigella*, sp., and *Entamoeba histolytica*) cause water-borne diseases like diarrhea, typhoid, and dysentery. The disinfection process is essential to use the pathogen contaminated water. Chemical processing (adding chlorine) of disinfection plays a vital role, but it forms a toxic chemical compound like haloacetic acids, chlorophenols etc. [54]. Alternatively, novel clay–polymer composites can be used as a disinfectant as it has the property of antimicrobial activity [40]. Copper-doped MMT low-density polyethylene nanocomposite prepared by Bruna et al. [14] shows 94% of antimicrobial activity and also kills 99% of *E. coli* in the contaminated water. This happens because the copper compounds degrade proteins and nucleic acids of microbial cell wall, which result in cell death [35]. Nanocomposite made up of clay–polymer–silver has higher antimicrobial activity over pathogens like *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Candida albicans*, and *E. coli*. So, it has been utilized in water treatment plant in commercial and residential complex [55]. Unuabonah et al. (2017) reported that steam regeneration technique for regenerating hybrid clay polymer membrane nanocomposites. The following is the major factors need to be maintained in an optimal level to obtain optimal activity of hybrid clay polymer membrane nanocomposites for the removal of pathogenic microbial community from wastewater are a. Adhesion property, b. Microbial characteristics, c. Flow conditions, d. Surface area and its charge, and e. Adsorbent hydrophobicity [57].

4.3 Removal of Pesticides and Heavy Metals Removal

Zadaka et al. [60] study the removal of pesticide atrazine and 2,4-dichlorophenol using clay polymer nanocomposites (MMT with poly-4-vinylpyridine-co-styrene), and the result shows that 99% of pesticide was removed from the water within 40 min. Gamiz et al. (2015) reported the removal of clopyralid and mecoprop using hexadimethrine–MMT nanocomposites through electrostatic attraction and found the removal efficiency is around 70%. Azzam et al. [10] formulated clay chitosan silver nanocomposites for the removal of Cu(II) ions from water, and result shows that maximum adsorption around 182 mg/g at pH 7.0 because the interaction of Cu(II) ions to chitosan is optimal at this pH. Khalek et al. prepared of poly/methacrylic acid attached with chitosan/bentonite nanocomposite for the removal of Hg(II), Cd(II), and Pb(II), and the removal efficiency in percentage is 94,78 and 89%, respectively. Khalek et al. also reported that for the removal of heavy metals happens at higher pH due to basic covalent bonding formation between heavy metal and surface of nanocomposites. On another study, 96% of Cu(II) ions and 99.5% of Pb(II) are removed from water stream by chemisorption process between clay/chitosan nanoparticles and heavy metals [33]. Table 2 shows some of the studies used nanocomposites for heavy metal removal and their adsorption capacity. Subsequently

Table 2 Nanocomposites for heavy metal removal

Clay-Nanocomposite	Water contaminants	Adsorption capacity (mg/g)	References
Chitosan/bentonite	Tartrazine	294.1	[57]
Chitosan/attapulgite	Cr (III)	65.37	[63]
Polyaniline modified bentonite	U(VI)	14.1	[36]
Chitosan/clinoptilolite	Ni (II)	247.5	[22]
Chitosan grafted poly acrylic acid bentonite composites	Cu (II)	88.6	[33]
Attapulgite/poly(acrylic acid)	Pb (II)	38	[38]

different modified clay-based nanocomposites membrane are used to remove metal and metalloids from wastewater. Montmorillonite (MMT) modified with N-methyl-D-glucamine-based monomer polymerized with ion-exchange resin the removal of arsenic.

Ravikumar et al. 2020 formulated bentonite clay and M. oleivera biopolymer to produce eco-friendly nanocomposites by the solution processing technique, and the same was utilized to removal of Cr (II), Pb (II), and Cd (II), from synthetic water contains 5 g/L of heavy metals, through coagulo-adsorption methodology, and maximum of 99.9% removal was achieved at pH range 5–7, 6–8, 2–4 Pb, Cd, Cr, respectively.

5 Conclusion

Clay hybrid membrane nanocomposites are utilized for the formulation of novel nanoparticles, and it shows a cost-effective sustainable removal of various contaminants industrial effluent by which helps to improve the environmental health. These clay membrane nanocomposites can be utilized in place of conventional treatment process for removal of heavy metals, pesticides, pathogens, organic and inorganic persisting chemical from various industrial effluent streams. Different researchers reported that removal of various contaminants industrial effluent stream using clay nanohybrid materials in laboratory scale using synthetic prepared effluent with different concentration of contaminants. But it is necessary for number of investigations to confirm the performance of clay hybrid membrane nanocomposites with real-time industrial wastewater stream which gives a route to formulate a pilot and large-scale treatment equipment for larger quantity of wastewater. On other hand, the innovative nanocomposites should be valued in account with various parameters associated to the nanoparticles properties (nanomaterial disposal and degradation, modification of surface chemical reaction, reuse or regeneration of nanocomposites and life cycle assessment). So, it helps to design a proper disposal mechanism for nanocomposites, when it enters into large-scale treatment process. Economic analysis needs to be studied to find benefit to cost ratio for feasible and sustainability use of clay hybrid membrane nanocomposites. Other challenges for the production and utilization of clay hybrid membrane nanocomposites needed a proper government policy at international and national levels to make best possible and proper use of clay hybrid membrane nanocomposites in association with knowledge of marketability.

References

1. Abbasian, M., Mahi, R.: In-situ synthesis of polymer – silica nanocomposites by living radical polymerisation using TEMPO initiator. J. Exp. Nanosci. **9**, 785–798 (2014). https://doi.org/10.1080/17458080.2012.714482
2. Ahmad, M.B., Gharayebi, Y., Salit, M.S., Hussein, M.Z., Shameli, K.: Comparison of In Situ polymerization and solution-dispersiontechniques in the preparation of polyimide/montmorillonite (MMT) nanocomposites. Int. J. Mol. Sci. **12**, 6040–6050 (2011). https://doi.org/10.3390/ijms12096040
3. Ahmad, T., Guria, C., Mandal, A.: Optimal synthesis and operation of low-cost polyvinyl chloride/bentonite ultrafiltration membranes for the purification of oilfield produced water. J. Membr. Sci. **564**, 859–877 (2018)
4. Al-Amshawee, S., Yunus, M.Y.B.M., Azoddein, A.A.M., Hassell, D.G., Dakhil, I.H., Hasan, H.A.: Electrodialysis desalination for water and wastewater: a review. Chem. Eng. J. **380**, 122231 (2020). https://doi.org/10.1016/j.cej.2019.122231
5. Ang, W.L., Mohammad, A.W., Hilal, N., Leo, C.P.: A review on the applicability of integrated/hybrid membrane processes in water treatment and desalination plants. Desalination **363**, 2–18 (2015)
6. Anirudhan, T.S., Suchithra, P.S., Radhakrishnan, P.G.: Synthesis and characterization app10072530 (2009)
7. Arya, V., Philip, L.: Adsorption of pharmaceuticals in water using Fe3O4 coated polymer clay composite. Microporous Mesoporous Mater. **232**, 273–280 (2016)
8. Ayalew, A.A.: A critical review on clay-based nanocomposite particles for application of wastewater treatment. Water Sci. Technol. **85**(10), 3002 (2022). https://doi.org/10.2166/wst.2022.150
9. Azha, S.F., Shamsudin, M.S., Shahadat, M., Ismail, S.: Low cost zwitterionic adsorbent coating for treatment of anionic and cationic dyes. J. Ind. Eng. Chem. **67**, 187–198 (2018)
10. Azzam, E.M.S., Eshaq, G., Rabie, A.M., Bakr, A.A., Abd-Elaal, A.A., El Metwally, A.E., Tawfik, S.M.: Preparation and characterization of chitosan-clay nanocomposites for the removal of Cu(II) from aqueous solution. Int. J. Biol. Macromol. **89**, 507–517 (2016)
11. Belachew, N., Bekele, G.: Synergy of magnetite intercalated bentonite for enhanced adsorption of Congo Red Dye. SILICON **12**, 603–612 (2020). https://doi.org/10.1007/s12633-019-00152-2
12. Bergaya, F., Detellier, C., Lambert, J.F., Lagaly, G.: Introduction to clay polymer nanocomposites (CPN). In: Bergaya, L. (ed.) Handbook of Clay Science. Developments in Clay Science, vol. 5. Elsevier, Amsterdam, The Netherlands
13. Bhatnagar, A., Sillanpää, M.: Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—a review. Chem. Eng. J. **157**, 277–296 (2010)
14. Bruna, J.E., Peñaloza, A., Guarda, A., Rodríguez, F., Galotto, M.J.: Development of MtCu 2+/LDPE nanocomposites with antimicrobial activity for potential use in food packaging. Appl. Clay Sci. **58**, 79–87 (2012)
15. Cainglet, A., Tesfamariam, A., Heiderscheidt, E.: Organic polyelectrolytes as the sole precipitation agent in municipal wastewater treatment, J. Environ. Manage. **271** (2020) https://doi.org/10.1016/j.jenvman.2020.111002

16. Chebotareva, R.D., Remez, S.V., Bashtan, S.Y.: Water softening and disinfection using an electrolysis unit with a filtering cartridge. J. Water Chem. Technol. **42**, 54–59 (2020). https://doi.org/10.3103/s1063455(20010026
17. Chen, D., Caruso, R.A.: Recent progress in the synthesis of spherical titania nanostructures and their applications. Adv. Func. Mater. **23**, 1356–1374 (2013). https://doi.org/10.1002/adfm.201201880
18. Cherifi, Z., Boukoussa, B., Zaoui, A., Belbachir, M., Meghabar, R.: Structural, morphological and thermal properties of nanocomposites poly (GMA)/clay prepared by ultrasound and in-situ polymerization. Ultrason. Sonochem. **48**, 188–198 (2018)
19. Couto, C.F., Santos, A.V., Amaral, M.C.S., Lange, L.C., de Andrade, L.H., Foureaux, A.F.S., Fernandes, B.S.: Assessing potential of nanofiltration, reverse osmosis and membrane distillation drinking water treatment for pharmaceutically active compounds (PhACs) removal. J. Water Process. Eng. **33**, 101029 (2020). https://doi.org/10.1016/j.jwpe.2019.101029
20. Daraei, P., Madaeni, S.S., Salehi, E., Ghaemi, N., Ghari, H.S., Khadivi, M.A., Rostami, E.: Novel thin film composite membrane fabricated by mixed matrix nanoclay/chitosan on PVDF microfiltration support: preparation, characterization and performance in dye removal. J. Memb. Sci. **436**, 97–108 (2013)
21. Dasgupta, J., Sikder, J., Chakraborty, S., Curcio, S., Drioli, E.: Remediation of textile effluents by membrane based treatment techniques: a state of the art review. J. Environ. Manag. **147**, 55–72 (2015)
22. Dinu, M.V., Dragan, E.S.: Evaluation of Cu 2þ, Co2þ and Ni 2þ ions removal from aqueous solution using a novel chitosan/clinoptilolite composite: kinetics and isotherms. Chem. Eng. J. **160**, 157–163 (2010). https://doi.org/10.1016/j.cej.2010.03.029
23. Drioli, E., Stankiewicz, A.I., Macedonio, F.: Membrane engineering in process enhanced swelling properties. Polym. Adv. Technol. **19**, 838–845 (2011)
24. Guo, F., Aryana, S., Han, Y., Jiao, Y.: A review of the synthesis and applications of polymer-nanoclay composites. Appl. Sci. (Switzerland) **8**, 1696 (2018). https://doi.org/10.3390/app8091696
25. Gurses, A.: Introduction to Polymer-Clay Nanocomposites. Pan Stanford, Singapore (2015)
26. Gámiz, B., Hermosín, M.C., Cornejo, J., Celis, R.: Hexadimethrine-montmorillonite nanocomposite: characterization and application as a pesticide adsorbent. Appl. Surf. Sci. **332**, 606–613 (2015)
27. Hubadillah, S.K., Othman, M.H.D., Ismail, A.F., Rahman, M.A., Jaafar, J.: A low cost hydrophobic kaolin hollow fiber membrane (h-KHFM) for arsenic removal from aqueous solution via direct contact membrane distillation. Sep. Purif. Technol. **214**, 31–39 (2019); Intensification—an overview. J. Membr. Sci. **380**(1–2), 1–8
28. Judd, S., Jefferson, B.: Membranes for industrial wastewater recovery and re-use (2003)
29. Jung-Hye, E.O.M., Young-Wook, K.I.M., Sung-Ho, Y.U.N., Song, I.-H.: Low-cost clay-based membranes for oily wastewater treatment. J. Ceram. Soc. Jpn. **122**(9), 788–794 (2014)
30. Kaya, A.U., Güner, S., Ryskin, M., Lameck, A.S., Benitez, A.R., Shuali, U., Nir, S.: Effect of microwave radiation on regeneration of a granulated micelle-clay complex after adsorption of bacteria. Appl. Sci. (Switzerland) **10**, 2530 (2020). https://doi.org/10.3390/app10072530
31. Kaya, A.U., Güner, S., Ryskin, M., Lameck, A.S., Benitez, A.R., Shuali, U., Nir, S.: Effect of microwave radiation on regeneration of a granulated micelle-clay complex after adsorption of bacteria. Appl. Sci. (Switzerland) **10**, 2530 (2020). https://doi.org/10.3390/
32. Khalil, A.M., Kenawy, S.H.: Hybrid membranes based on clay-polymer for removing methylene blue from water. Acta Chim. Slov. **67**, 96–104 (2020). https://doi.org/10.17344/acsi.2019.5227
33. Kumararaja, P., Manjaiah, K.M., Datta, S.C., Shabeer, A.T.P., Sarkar, B.: Chitosan-g-poly(acrylic acid)-bentonite composite: a potential immobilizing agent of heavy metals in soil. Cellulose **25**, 3985–3999 (2018)
34. LeBaron, P.C., Wang, Z., Pinnavaia, T.J.: Polymer-layered silicate nanocomposites: an overview. Appl. Clay Sci. **15**, 11–29 (1999)

35. Lejon, D.P.H., Pascault, N., Ranjard, L.: Differential copper impact on density, di-versity and resistance of adapted culturable bacterial populations according to soil organic status. Eur. J. Soil Biol. **46**, 168–174 (2010)
36. Liu, X., Cheng, C., Xiao, C., Shao, D., Xu, Z., Wang, J., Hu, S., Li, X., Wang, W.: Polyaniline (PANI) modified bentonite by plasma technique for U(VI) removal from aqueous solution. Appl. Surf. Sci. **411**, 331–337 (2017). https://doi.org/10.1016/j.apsusc.2017.03.095
37. Liu, P., Jiang, L., Zhu, L., Guo, J., Wang, A.: Synthesis of covalently cross linked attapulgite/poly(acrylic acid-co-acrylamide) nanocomposite hydrogels and their evaluation as adsorbent for heavy metal ions. J. Ind. Eng. Chem. **23**, 188–193 (2015)
38. Liu, X., Lee, D.J.: Thermodynamic parameters for adsorption equilibrium of heavy metals and dyes from wastewaters. Biores. Technol. **160**, 24–31 (2014). https://doi.org/10.1016/j.biortech.2013.12.053
39. Liu, Y., Takafuji, M., Ihara, H., Wakiya, T.: Saturation magnetization of inorganic/polymer nanocomposites higher than that of their inorganic magnetic component (2012). arXiv:1206.2805
40. Madkour, A.E., Dabkowski, J.M., Nüsslein, K., Tew, G.N.: Fast disinfecting antimicrobial surfaces. Langmuir **25**, 1060–1067 (2009)
41. Mahdavinia, R.Z., Baghban, A., Zorofi, S., Massoudi, A.: Kappa-carrageenan bipolymer-based nanocomposite hydrogel and adsorption of methylene blue cationdye from water. J. Mater. Environ. Sci. **5**(2), 330–337 (2014)
42. Mahdis, H., Azam, J.-A.: Morphology development via static crosslinking of (polylactic acid/acrylic rubber) as an immiscible polymer blend. Macromol. Mater. Eng. **303**, 1700446 (2018)
43. Meyer, D.E., Upadhyayula, V.K.K.: The use of life cycle tools to support decision making for sustainable nanotechnologies. Clean Technol. Environ. Policy **16**, 757–772 (2014). https://doi.org/10.1007/s10098-013-0686-3
44. Moustafa, H., Galliard, H., Vidal, L., Dufresne, A.: Facile modification of organoclay and its effect on the compatibility and properties of novel biodegradable PBE/PBAT nanocomposites. Eur. Polym. J. **87**, 188–199 (2017)
45. Mukhopadhyay, R., Bhaduri, D., Sarkar, B., Rusmin, R., Hou, D., Khanam, R., Sarkar, S., Kumar Biswas, J., Vithanage, M., Bhatnagar, A., Ok, Y.S.: Clay–polymer nanocomposites: progress and challenges for use in sustainable water treatment. J. Hazard. Mater. **383**, 121125 (2020). https://doi.org/10.1016/j.jhazmat.2019.121125
46. Naidu, R., Biswas, B., Willett, I. R., Cribb, J., Kumar Singh, B., Paul Nathanail, C., Coulon, F., Semple, K. T., Jones, K. C., Barclay, A., John Aitken, R.: Chemical pollution: a growing peril and potential catastrophic risk to humanity. Environ. Int. **156**, 106616 (2021). https://doi.org/10.1016/j.envint.2021.106616
47. Rane, A.V., Kanny, K., Abitha, V.K., Patil, S.S., Thomas, S.: Clay–polymer composites: design of clay polymer nanocomposite by mixing. In: Clay-Polymer Nanocomposites; Elsevier: Amsterdam, The Netherlands, pp. 113–144 (2017)
48. Ravikumar, K., Udayakumar, J.: Preparation and characterisation of green clay-polymer nanocomposite for heavy metals removal. Chem Ecol. **36**, 270–291 (2020)
49. Siddeeg, S.M., Tahoon, M.A., Rebah, F.B.: Simultaneous removal of calconcarboxylic acid, NH4þ and PO43- from pharmaceutical effluent using iron oxide-biochar nanocomposite loaded with Pseudomonas putida. Processes **7**, 800 (2019). https://doi.org/10.3390/pr7110800.
50. Skaf, D.W., Punzi, V.L., Rolle, J.T., Kleinberg, K.A.: Removal of micron-sized microplastic particles from simulated drinking water via alum coagulation. Chem. Eng. J. **386**, 123807 (2020). https://doi.org/10.1016/j.cej.2019.123807.Verma&Balomajumder2020
51. Theron, J., Walker, J.A., Cloete, T.E.: Nanotechnology and water treatment: applications and emerging opportunities. Crit. Rev. Microbiol. **34**, 43–69 (2008). https://doi.org/10.1080/10408410701710442
52. Tokarcíková, M., Tokarský, J., Kutláková, K.M., Seidlerová, J.: Testing the stability of magnetic iron oxides/kaolinite nanocompounder various pH conditions. J. Solid State Chem. **253**, 329–335 (2017). https://doi.org/10.1016/j.jssc.2017.06.004

53. Tom, A.P.: Nanotechnology for sustainable water treatment – a review. Mater. Today: Proc. (2021). ISSN 2214-7853. https://doi.org/10.1016/j.matpr.2021.05.629
54. Undabeytia, T., Posada, R., Nir, S., Galindo, I., Laiz, L., Saiz-Jimenez, C., Morillo, E.: Removal of waterborne microorganisms by filtration using clay–polymercomplexes. J. Hazard. Mater. **279**, 190–196 (2014)
55. Unuabonah, E.I., Taubert, A.: Clay–polymer nanocomposites (CPNs): adsorbents of the future for water treatment. Appl. Clay Sci. **99**, 83–92 (2014)
56. Unuabonah, E.I., Ugwuja, C.G., Omorogie, M.O., Adewuyi, A., Oladoja, N.A.: Clays for efficient disinfection of bacteria in water. Appl. Clay Sci. **151**, 211–223 (2018)
57. Wan Ngah, W.S., Ariff, N.F.M., Hashim, A., Hanafiah, M.A.K.M.: Malachite green adsorption onto chitosan coated bentonite beads: isotherms, kinetics and mechanism. Clean – Soil Air Water **38**, 394–400 (2010)
58. Wang, L., Zhang, J., Wang, A.: Removal of methylene blue from aqueous solution using chitosan-g-poly(acrylic acid)/montmorillonite super adsorbent nanocomposite. Colloids Surf. A Physicochem. Eng. Asp. **322**, 47–53 (2008)
59. Yano, K., Usuki, A., Okada, A.: Synthesis and properties of polyimide-clay hybrid films. J. Polymer Sci. Part A, **35**, 2289–2294 (1997)
60. Zadaka, D., Nir, S., Radian, A., Mishael, Y.G.: Atrazine removal from water by polycation–clay composites: effect of dissolved organic matter and comparison to activated carbon. Water Res. **43**, 677–683 (2009)
61. Zang, L., Qiu, J., Yang, C., Sakai, E.: Preparation and application of conducting polymer/Ag/clay composite nanoparticles formed by in situ UV-induced dispersion polymerization. Sci. Rep. **6**, 20470 (2016)
62. Zhu, Y., Chen, D.: Novel clay-based nanofibrous membranes for effective oil/water emulsion separation. Ceram. Int. **43**, 9465–9471 (2017)
63. Zou, X., Pan, J., Ou, H., Wang, X., Guan, W., Li, C., Yan, Y., Duan, Y.: Adsorptive removal of Cr(III) and Fe(III) from aqueous solution by chitosan/attapulgite composites: equilibrium, thermodynamics and kinetics. Chem. Eng. J. **167**, 112–121 (2011). https://doi.org/10.1016/j.cej.2010.12.009

Clay-Supported Nanoscale Zero-Valent Iron Composites for Water Purification

Yasmitha A. Alahakoon, Uthsara Malaweera Arachchi, and Sameera R. Gunatilake

Abstract Anthropogenic water pollution has resulted in increased concentrations of aquatic contaminants that can be toxic to human health and the environment. In recent years, the development and application of nanoscale zero-valent iron (nZVI) for water purification have gained interest due to its non-toxic nature and inexpensiveness. Contaminant remediation properties of nZVI are mostly due to its strong reducing power which allows the sequestration and degradation of pollutants through advanced oxidative processes (AOP) and reductive mechanisms. Attention has been paid to clay-supported nZVI materials (C-nZVI) as efficient remediation agents in wastewater and groundwater treatment. Composites of C-nZVI possess superior benefits over individual pristine components, such as rapid sorption, reduced iron leaching and recyclability. Nanocomposites can be engineered using various materials such as polymers, carbonaceous material and metals in synergy with clays and nZVI to produce novel composites with unique properties. In general, remediation by C-nZVI is at its highest in mild acidic conditions due to increased catalytic activity. The surface charge of the clay mineral also plays an important role in contaminant remediation. C-nZVI associated free radical mediated AOPs facilitate remediation without any additional heat or light energy. This chapter reviews the recent advances in contaminant remediation by C-nZVI including material synthesis, mechanisms, properties and advantages.

Keywords Nanoscale zero-valent iron · Clay composites · Water remediation · Advanced oxidative processes

---

Y. A. Alahakoon · U. Malaweera Arachchi · S. R. Gunatilake (✉)
College of Chemical Sciences, Institute of Chemistry Ceylon, Rajagiriya CO 10107, Sri Lanka
e-mail: ranmal@ichemc.edu.lk

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_21

1 Introduction

Severe global water scarcity due to exponential increase in the world population has caused grave challenges [1]. Contamination of natural water sources by organic and inorganic pollutants has drastic impacts in the ecological, economic and environmental context [1, 2]. Water contamination can occur naturally and through anthropogenic activities. Natural sources can potentially contaminate water. For instance, arsenic contamination can occur due to weathering of arsenic-containing rocks [3]. Anthropogenic pollution of water is predominantly caused by industrial, agricultural, commercial and domestic means [3, 4].

To alleviate this issue, there is a constant focus on treating and recycling polluted water before its subsequent release to the environment. A broad range of physical, chemical and biological processes have been used for wastewater treatment [1, 4–6]. Out of these, the application of nanomaterials in water purification has been explored to a great extent throughout the past decade [1]. Nanomaterials encompass a range of special features such as high reactivity, high porosity, catalytic potential, compact size and large surface area to volume ratio which allow them to work rapidly with increased adsorption than conventional materials [5, 6]. They also have the advantage of reusability after chemical regeneration of the material [5]. The salient properties essential for any engineered nanoparticle used for in-situ remediation are adequate reactivity, mobility, reactive longevity and low toxicity [6].

A lot of attention has been paid to the development and application of nanoscale zero-valent iron (nZVI) in water purification in recent years. Iron is a relatively non-toxic and inexpensive metal. It is the most abundant transition metal on earth. The versatility of remediation properties of zero-valent iron are mainly due to its low standard redox potential of −0.44 V which gives it a fairly strong reducing power [7–9]. It also allows it to sequester and degrade contaminants through reductive mechanisms and advanced oxidative processes (AOP) such as Fenton-type reactions [10]. A typical Fenton reaction is a process where hydroxyl radicals are generated through the catalytic reaction of oxidizing Fe(II) to Fe(III) with hydrogen peroxide. In this reaction, Fe(II) acts as the reaction catalyst [11]. Sludge formation is reduced in Fenton-type reactions of nZVI as the Fe(III) produced reacts continuously with Fe(0) to generate a steady supply of Fe(II) for the function of the Fenton process [12]. Superior characteristics of nanoparticles listed before are possessed by nZVI, in contrast to its micro- and macroscale counterparts [3].

The synthesis of nZVI can be carried out using three main paths, namely physical, chemical and green synthesis [4]. Gas condensation processing and ball milling are considered as physical methods while liquid phase reduction, ultrasound-assisted synthesis, carbothermal synthesis, thermal decomposition, chemical vapor condensation, hydrothermal method, polyol process and electrochemical methods can be categorized as chemical methods [4]. Green synthesis is carried out using polyphenol-rich natural product extracts from various plant materials to be used as both reducing and capping agents for nZVI [13].

Despite the unique properties of nZVI, the pristine material has several drawbacks that can limit its potential. Bare nZVI is prone to rapid agglomeration, sedimentation and passivation which can result in the reduction of effective surface area, mobility and Fenton reactivity [3, 4]. Long term storage of bare nZVI is also not sustainable due to rapid oxidation which requires them to be used right after production for best efficiency. Intense agglomeration is brought about by strong magnetic attractive properties, reactivity and high surface energy of nZVI. Formation of oxide and hydroxide layers as corrosion products of oxidation hinder the zero-valent core of nZVI and are responsible for rapid passivation [10].

The aforementioned limitations can be overcome by supporting nZVI on solid carriers. Literature reports the use of polymers, carbonaceous materials, clay minerals, zeolites, humic substances and other materials such as dietary fibers, cation exchange membranes, calcium-alginate beads and silica fume as supports for nZVI [14, 15].

Clay minerals have been well documented in their function as solid support materials for pristine nZVI owing to their enhanced adsorption properties, stability, biocompatibility, non-toxic and green nature, natural abundance and low cost [1, 16]. Clays can disperse nZVI on their surface, inhibiting aggregation, providing a longer shelf life and reduced leaching [17–19].

To date, several high-quality reviews have been published on the remedial action of clay-based adsorbents as well as nZVI-based composites, in which clay-supported nZVI materials (C-nZVI) have been discussed [5, 12, 15, 20]. In addition, the synthesis and removal mechanisms of C-nZVI have been comprehensively reviewed [1, 9]. However, to the best of our knowledge, recent studies on C-nZVI-based remediation, novel engineered C-nZVI composites (eC-nZVI) and remedial mechanisms in free radical mediated AOPs have not been thoroughly reviewed as of yet.

This chapter attempts to bridge this gap by providing a thorough insight into the recent advances of eC-nZVI from 2017 to present (2022). Properties of clays in C-nZVI composites, material preparation methods, remedial mechanisms and specific advantages of C-nZVI published during the past five years have been comprehensively reviewed. Specific attention has been given to eC-nZVI materials and the remedial action of free radical mediated AOPs. The contents and conclusions presented in this work will aid and facilitate a sagacious planning process for future studies on C-nZVI.

2 Clay Minerals Used in C-nZVI Materials

Clay minerals are mainly classified based on their contrasting layered structures, exchangeable ions, particle sizes and the type of substituted metals [1]. Silicate minerals which make up most of the earth's crust, are the largest and most important class of minerals. They can be mainly classified into phyllosilicates and tectosilicates [21].

Clay minerals are mainly phyllosilicates [22]. They have a basic structure consisting of polymerized tetrahedral sheets (T) of silica made of $Si_2O_6(OH)_4$ units and octahedral sheets (O) of alumina composed of $Al_2(OH)_6$ units. Isomorphic substitution in the tetrahedral sheets and/or in the octahedral sheets of clay minerals results in negative surface charges of clay minerals [23]. These charges are balanced by naturally occurring cations which exist in the inter-layers or on the clay surface. This paves the way to saturate smectites with iron cations which can be reduced to nZVI [24].

Phyllosilicates can be further classified into layer silicates and chain silicates. Based on the manner of arrangement of these layer silicates, they can be categorized as 1:1 (T-O) and 2:1 (T-O-T) phyllosilicates. In 1:1 phyllosilicates, there is one tetrahedral sheet for every octahedral sheet whereas 2:1 phyllosilicates are composed of one octahedral sheet sandwiched between two tetrahedral sheets. Kaolinite and halloysite clays have 1:1 composition, while smectite, mica, illite and vermiculite clays have 2:1 composition. The smectite group of clay minerals are further grouped into trioctahedral saponites and dioctahedral montmorillonite [23]. It also consists of secondary minerals like quartz and calcite [25].

The structures of sepiolite and palygorskite are similar, consisting of narrow ribbons of 2:1 layers that are attached to each other at the corners. The ribbon width defines the number of octahedral cation positions per formula unit. These clays are classified under chain silicates [20, 23].

Zeolites are a type of tectosilicates used to form nanocomposites with nZVI. Tectosilicates are a class of silicates with a continuous three-dimensional framework of tetrahedral silicates. With the objective of giving the reader, a wider scope into other silicates popularly used in forming nZVI composites, zeolite-based nZVI composites (Zeol-nZVI) have also been included in this chapter.

2.1 Layer Silicates

2.1.1 1:1 Type Layer Silicates

Several C-nZVI studies have been carried out using 1:1 layered kaolinite. However, less attention has been paid to the utilization of halloysite as a clay support for nZVI in recent studies which may be due to its low cation exchange capacity that results in less uptake of contaminants [20].

Kaolinite: Kaolinite can form as a result of chemical weathering of aluminum silicate minerals such as feldspar. It is a layered silicate mineral with one tetrahedral silica sheet linked through an apical oxygen to one octahedral alumina sheet. These layers can be joined as sheets to other layers, forming a large set of clay layers. Since kaolinite layers have no net electrical charge on them, no large cations can be found between the layers, which accounts for the relatively low ion exchange capacity of kaolinite compared to other clay minerals. Infiltration of water molecules into the layers are also hindered in kaolinite due to the close hydrogen bonding between layers, which is indicated by the non-swelling character of the mineral [26]. However, kaolinite could potentially be used as a porous-based material to support nZVI for the removal of metal ion contaminants in aqueous media [27].

2.1.2 2:1 Type Layer Silicates

Recent studies on C-nZVI have focused predominantly on bentonite and montmorillonite which belong to the dioctahedral smectite family [24, 28, 29]. Smectites are very effective at attenuating many organic and inorganic pollutants because of their high surface area and adsorptive properties. Smectites have a shrink-swell behavior, where they shrink when dry and swell when wet. This mineral is naturally available, cost effective and biocompatible in natural systems [1].

Montmorillonite: Montmorillonite minerals are products of volcanism and hydrothermal activity and usually occur in regions with poor drainage. Based on the inter-layer ion species, naturally occurring montmorillonite is classified as Na-montmorillonite or Ca-montmorillonite. Out of the two, Na-montmorillonite has better performance as a result of the lower hydration energy of cation. The adequate inter-layer spaces of the layered structure of montmorillonite provide good support for nZVI particles [30]. Due to its permanent negative surface charge, it has a high cation exchange capacity and good adsorption properties, allowing it to be used in the treatment of metal ions and cationic organic contaminants in wastewater [31–33].

Bentonite: Another important member of the smectite group is bentonite which is an aluminum phyllosilicate clay consisting of Na-montmorillonite as its main component along with other impurities such as kaolinite, quartz, feldspar and calcite [34–37]. Bentonite is commonly found in the bottom and sides of ponds, waste lagoons and landfills. It is a swelling clay and a traditional economic adsorbent with high specific surface area formed by modifications of minuscule glass particles derived from volcanic ash. Bentonite is a good carrier due to its ability to swell and maintain a uniform dispersion in water [36]. Fine dispersion of nZVI reactive nanodomains on bentonite surface leads to low aggregation which results in increased sorption rates [18, 30]. Reduced iron oxide shell formation due to continuous uptake of dissolved iron species by the clay substrate leads to lower nZVI burnout and inactivation [18]. Furthermore, bentonite supported nZVI (Bent-nZVI) has reduced hydrophobicity which facilitates remediation in aqueous media [18]. Bent-nZVI is widely used in the remediation of a variety of organic contaminants, oxyanions and heavy metals [18, 36, 38, 39].

Vermiculite: A mica-like trioctahedral silicate clay mineral with a 2:1 layered structure. It is mostly produced by the removal of potassium from biotite, phlogopite, or muscovite [40]. Vermiculite supported nZVI (Verm-nZVI) has been reported in the remediation of Cr(VI) [41].

2.1.3 Mixed Layer Clay Minerals

Clay minerals such as illite and rectorite are composed of two or more different kinds of institutional unit sheets and are referred to as mixed-layer clay minerals [42].

Rectorite: Rectorite clay is made up of a 1:1 mixture of non-expandable dioctahedral mica and expandable dioctahedral smectite layers. It is a well-stratified silicate material with a more stable structure than that of montmorillonite [43]. It is also a cost effective and an easily obtainable material. Rectorite possesses multiple advantages such as high mechanical and thermal resistance, good water colloidal properties and the presence of exchangeable ion species [44]. Compared to montmorillonite, rectorite might be an even better candidate for pillared structures [45].

2.2 Chain Silicates

Chain silicates have a 2:1 layer basic structure unit composed of continuous tetrahedral sheets and discontinuous octahedral sheets as well as a fiber-shaped crystal morphology. Palygorskite and sepiolite are chain silicates that have been widely used in the synthesis of C-nZVI. Palygorskite has a rod shaped 2:1 layer-chain structure, while sepiolite possesses a 2:1 layer fiber-shaped chain structure [46, 47]. These chain structures have crystallographic defects resulting from the replacement of Mg(II) ions in octahedral sites by trivalent cations like Al(III) and Fe(III). The defects lead to the formation of surface negative charge and structural negative charge [46].

Palygorskite: Palygorskite or attapulgite is a magnesium aluminosilicate mineral with a higher water absorption capacity. This mineral occurs in calcareous material, desert soils and sediments from playa lakes and saline deposits. Presence of numerous deposits, lower price and relatively high surface area makes attapulgite a noteworthy clay mineral. It is a 2:1 type natural clay mineral which has a large number of silanol groups at the edge sites, facilitating the heavy metal adsorption. According to literature, palygorskite is a potential adsorbent for various heavy metals and some researchers have developed palygorskite supported nZVI composites (Pal-nZVI) with better contaminant removal efficiencies [48].

Sepiolite: Sepiolite is a naturally abundant low-cost clay mineral with a stable structure and is very abundant in the black sea region. It consists of hydrated magnesium silicate, and it is structurally similar to the layered clay mineral montmorillonite [49]. It possesses a micro-fibrous morphology with a high specific surface area, which gives the mineral a remarkable effectiveness in removing contaminants. Sepiolite is employed as a supporting substance to improve the dispersion of nZVI nanoparticles as homogenous dispersion of nZVI in aqueous solutions can enhance their effectiveness [50].

2.3 Zeolite

Zeolite is a hydrated aluminosilicate mineral with a linked tetrahedral framework, each containing a silicon or aluminum cation with four surrounding oxygen atoms. Extensive deposits of zeolites occur in oceans, mafic volcanic rock and sedimentary rocks of marine origin. The three-dimensional structure of zeolite has open cavities, which are large enough to pass through guest ionic and molecular species. Therefore, certain zeolites are capable of exchanging cations and acting as molecular sieves. Zeolites are commonly used as adsorbents for various contaminants as they are known to have a high sorption capacity for inorganic pollutants [51]. Researchers have found zeolite to be an effective dispersant and a stabilizer of nZVI in composite support systems, resulting in reduced aggregation and increased specific surface area.

3 Clay Incorporated nZVI Materials

3.1 Synthesis of Clay-Supported nZVI Composites

Standard methods of nZVI synthesis have been well documented [52]. Majority of the reported studies on C-nZVI have employed liquid phase reduction via $NaBH_4$ for the synthesis of nZVI. Both ferrous and ferric salts with different counter ions such as SO_4^{2-}, NO_3^-, Cl^- have been used as the iron source [30, 48, 53]. In addition, a few studies out of those selected have used the green synthesis method where polyphenol-rich extracts from natural plant sources such as green tea, eucalyptus leaves and pomegranate rinds are used as the reducing and stabilizing agent of nZVI in simple clay nZVI composite synthesis [54–56].

According to the articles considered, the two approaches to C-nZVI composite synthesis are (1) mixing clay with an iron salt with subsequent reduction to Fe(0) and (2) reducing the iron salt to Fe(0) with subsequent deposition on the clay surface [29, 31, 55, 57]. Apart from a very few reported studies, the rest have utilized the first approach for the synthesis.

Yin et al. have fabricated Montmorillonite supported nZVI (Mont-nZVI) using liquid phase reduction and depositing them on the clay surface. Reducing the iron salt before adhering on to the carrier makes the nZVI particles deposit on the surface as a monolayer. The synthesized material demonstrated much higher remediation efficiency for Cr(VI) than agglomerated pristine nZVI. However, when pristine nZVI particles were monodispersed under sonication, remediation capacity was observed to be similar to the synthesized C-nZVI. It has been observed that depending on different experimental conditions, the size and the concentration of the attached nZVI particles on the carrier surface could be controlled [31]. Baldermann et al. have used a suspension of nZVI to prepare Bent-nZVI for the remediation of trichloroethane. The suspension has been subjected to ultrasonic treatment to prevent the particle agglomeration before depositing on the clay surface [18].

In the synthesis process, the clay: Fe(0) ratio could be a crucial factor for the attributed properties of the final material. In a study, Wu et al. have compared the sulfamethazine degradation efficiencies using organo-Mont-nZVI. Different mass ratios of nZVI to clay were incorporated where the remediation efficacy increased up to a certain level with the increasing mass of the carrier due to better dispersion of nZVI particles. Beyond this optimum level, a decreased efficiency was observed which could be due to blockage of the reactive nZVI sites with any excess carrier added [33]. Similar observations were reported for Pal-nZVI and amino functionalized Verm-nZVI [41, 58]. Furthermore, the aggregation of clay sheets when excess clay is added has been documented as a cause for the diminished surface area and catalytic activity of the composite [58].

Ding et al. have also synthesized Pal-nZVI composites varying the nZVI to clay ratio to remediate quinclorac in a peroxymonosulfate system. It has been seen that if nZVI is increased beyond a certain amount, the remediation efficiency will slightly decrease owing to the radical scavenging activity of Fe(II) (explained in Sect. 4.4.1) which will limit the formed hydroxyl and sulfate radical concentration in the medium. Precipitation of iron species and accumulation of by-products from the degradation process on the Pal-nZVI surface will also result in lesser performance of the material [58].

Clay varieties, bearing different intrinsic properties can have a substantial impact on the removal efficiency of a particular composite. A study by Kornilovych et al. targeting the remediation of Uranium species utilizing three different clays, have proven that Mont-nZVI has the highest removal efficiency, while Pal-nZVI and Kaol-nZVI have moderate and lowest efficiencies, respectively. The stated sequence can be attributed to the decrease in surface area of pristine clay minerals [53].

3.2 Advantages of Clay-Supported nZVI Composites

C-nZVI possesses exceptional benefits over both pristine nZVI and pure clays when compared individually. Different types of clays can be synergistically combined with nZVI to produce C-nZVI composites that have enhanced properties of both components.

When compared with pristine nZVI, the following specific advantages have been observed when nZVI is loaded onto clays. Numerous studies have reported fine dispersion and speckled morphology of nZVI when supported on clay substrates in contrast to the aggregation of bare material [18, 30]. Phyllosilicates lead to rapid sorption of adsorbates owing to their reactive sites. High degradation rate of contaminants by C-nZVI increases the accessibility of new reaction sites [30]. In addition, leaching of metallic contaminants which are reduced to their zero-valent state by nZVI can be prevented by subsequent co-precipitation on the clay surface [17]. As observed by Bao et al. for Bent-nZVI, sludge formation due to iron leaching associated with traditional Fenton-type reactions can be minimized by C-nZVI materials [30].

The buffer action of aluminol or silanol groups on clays can minimize fluctuation in pH of C-nZVI reaction systems when compared to bare nZVI [59, 60]. Li et al. reported the buffered pH of Al-Bent-nZVI and Na-Bent-nZVI to be 6.7 and 7.3 in comparison to 7.7 in bare nZVI when the initial pH was 6.0. Composites operating under a nearly neutral buffered pH show decreased production of insoluble iron oxides on the surface of nZVI and facilitates electron transfer from nZVI core to the surface [59]. Soliemanzadeh et al. observed that inner-sphere binding and covalent bonds of phosphorus anions led to less irreversibility of sorption by Bent-nZVI [54]. Desorption of adsorbed contaminants on natural clays is mitigated by contaminant degradation facilitated by the loaded nZVI [54]. Sorption of contaminants was seen to be less reversible on C-nZVI than on natural clays as a result of strong interactions. The inherent magnetic properties of nZVI allow magnetic separation and recovery of the nanocomposite post-remediation, in a less time consuming and hassle-free manner in contrast to inefficient recovery of pure clays [41, 61]. Formation of nanocomposites also helps reduce particle toxicity that arises from the difficulty in recycling pristine nZVI due to their small size [60].

In this chapter, nanocomposites which have been synthesized using only clay and nZVI are referred to as ‘simple clay nZVI composites’ (sC-nZVI), whereas materials which have been synthesized using other novel components synergistically with clay and nZVI have been designated as ‘engineered clay nZVI materials’ (eC-nZVI). These composites which have engineered materials in conjunction with clays have added benefits in addition to the common advantages of all C-nZVI.

3.3 Engineered C-nZVI Materials

Engineering nanocomposites using materials such as polymers, carbonaceous materials and other metals in combination with nZVI and clays produces novel composites with unique, superior properties. Accelerated and long-lasting Fenton activity, higher reusability, enhanced hydrophobicity, longer shelf life, broad effective pH range, better adsorption, redox mediation and introduction of positive charges on material surface are special characteristics observed in these engineered materials [17, 62–64]. Furthermore, materials have been engineered by incorporating the combined effects of membrane filtration and remediation through Fenton activity. A summary of contaminant remediation by eC-nZVI has been provided in Table 1.

3.3.1 Bimetallic C-nZVI Materials

Bimetallic C-nZVI composites are unique in their utilization of nZVI in concomitance with another zero-valent metal such as Cu, Ni and Pd. These materials have enhanced catalytic activity due to radical H-formation and better stability when compared with C-nZVI. The concerted action of the metal added with nZVI has been

Table 1 Summary of engineered clay-supported nZVI composites for contaminant remediation

Type	Incorporation	Support	Contaminant	Role of the incorporation	Outcome	Refs.
Carbonaceous	Activated charcoal	Bentonite	Methylene blue, Rhodamine B	Providing porosity to form a layered-porous morphology	Long shelf life	[62]
Carbonaceous	Biochar	Bentonite	Ni(II), Cr(VI), Methylene blue	Providing porosity to form a layered-porous morphology. To add surface functionality to provide a good attaching platform	Enhanced adsorption properties	[17]
Carbonaceous	Graphene oxide	Bentonite	Cu(II)	Providing porosity to form a layered-porous morphology. To add surface functionality to provide a good attaching platform	Enhanced adsorption properties	[36]
Carbonaceous	Reduced graphene oxide	Palygorskite	Acid Red 18 dye	Providing porosity to form a layered-porous morphology. To add surface functionality to provide a good attaching platform	Enhanced adsorption properties. Long shelf life	[19]
Carbonaceous	Graphitic carbon nitride	Palygorskite	Methylene blue	Production of photo-generated electrons to regenerate consumed Fe(0)	Preserved nZVI reactivity	[68]

(continued)

Table 1 (continued)

Type	Incorporation	Support	Contaminant	Role of the incorporation	Outcome	Refs.
Polymer	Polydopamine	Palygorskite	Cr(VI)	Redox mediation, donation of electrons to the contaminant, serving as an organic ligand	Accelerated reduction of the contaminant. Facilitates the reduction of Fe(III) to Fe(II). Prevents leaching of iron	[64]
Polymer	Polypyrrole	Palygorskite	Naphthol green B	Promoting ion exchange and electrostatic interaction due to positively charged nitrogen atoms. Providing protective effect from polypyrrole-Pal layers	Enhanced adsorption properties. Preserved nZVI reactivity	[63]
Polymer	Carboxymethyl chitosan	Bentonite	Crystal violet, Congo red	Promoting ion exchange and electrostatic interactions due to positively and negatively charged functional groups under different pH conditions	Enhanced adsorption properties. Broad working pH range	[69]
Polymer	Polyethylene glycol	Zeolite	Fluoroquinolone antibiotics	Acting as a dispersing agent	Restrained magnetic activity among the nZVI particles. Higher reactivity	[61]
Polymer	Polyethersulfone	Kaolinite	As(III)	Enhancing oxidative and mechanical properties	Efficient contaminant remediation	[70]
Bimetallic	Cu	Bentonite	Tetracycline	Acting as a catalyst to prevent iron oxidation	Enhanced stability of nZVI	[55]

(continued)

Table 1 (continued)

Type	Incorporation	Support	Contaminant	Role of the incorporation	Outcome	Refs.
Bimetallic	Ni	Zeolite	Trichloroethene	Acting as a catalyst to regenerate Fe(II) from Fe(III) via formed Ni(I). Generation of hydroxyl radicals from hydrogen peroxide	Accelerated degradation of trichloroethene Stabilization of iron. Activation of percarbonate systems	[65]
Bimetallic	Ni	Palygorskite	2,4-dichlorophenol	Acting as a hydrogen catalyst to dissociate H_2 and generate hydrogen radicals	Enhanced dechlorination of the contaminant	[60]
Bimetallic	Pd	Organo palygorskite	Decabromodiphenyl ether	Acting as a hydrogen catalyst to dissociate H_2 and generate hydrogen radicals	Enhanced debromination of the contaminant	[66]
Bimetallic	Ni	Zeolite	Heavy metals	Acting as an electron carrier as well as a catalyst to generate atomic hydrogen	Improved reductive immobilization of heavy metals facilitated by the improvement of electron donor ability of nZVI	[67]
Other	MCM-41	Zeolite	Tetracycline	Introducing enhanced porosity and large surface area	Improved adsorption capacity and hydrothermal stability	[71]

reported to aid the continued redox activity of oxidized iron by reducing generated Fe(III) to Fe(II) which can then be reused as a reducing agent [55, 60, 65].

Copper could be used as a catalytic additive to C-nZVI composites on account of its signature properties. Gopal et al. synthesized Cu(0) incorporated green Bent-nZVI which portrays enhanced stability of nZVI, regeneration after remediation via convenient separation and substantial prevention of iron oxidation [55]. Accelerated degradation of trichloroethene based on the thermodynamic feasibility of regenerating Fe(II) from Fe(III) via formed Ni(I) in the Ni(0) incorporated Zeol-nZVI composite has been reported by Danish et al. [65].

Ezzatahmadi et al. produced a Pal-nZVI composite with added Ni(0) as a catalyst to remediate 2,4-dichlorophenol. Molecular hydrogen produced by the corrosion of nZVI was rapidly converted to hydrogen radicals by the catalytic activity of Ni(0), which caused enhanced dechlorination of the molecule [60]. Similar catalytic mechanism was observed for Pd(0) incorporated organo-Pal-nZVI in the debromination of decabromodiphenyl ether [66].

Application of bimetallic C-nZVI materials for heavy metal removal is also documented. Incorporation of Ni(0) in Zeol-nZVI was studied by Angaru et al. Here, Ni(0) acts as an electron carrier as well as a catalyst to generate atomic hydrogen which facilitates the improvement of electron donor ability of nZVI causing the improved reductive immobilization of heavy metals [67].

3.3.2 Carbonaceous Materials Incorporated C-nZVI Materials

Literature reports the utilization of several carbonaceous materials such as activated charcoal, biochar (BC), graphene oxide (GO), reduced GO (rGO) and graphitic carbon nitride (GCN) in the preparation of clay incorporated engineered nZVI materials [17, 19, 36, 62].

Khandelwal et al. showed that activated charcoal incorporated Bent-nZVI provided a layered-porous surface which preserved nZVI reactivity even after a 300-day exposure to open air [62]. In a different study, Khandelwal et al. presented a clay BC composite supported nZVI material which gave enhanced adsorption properties due to the porous structure and functionality of BC. Economical and abundant raw materials were used in the simple and easier synthesis [17].

The removal of copper has been improved by the use of GO as an additive in Bent-nZVI. Efficient remediation was due to the strong adsorption properties of hydrophilic GO which was uniformly dispersed under ultrasonication. Furthermore, the authors have credited the large specific surface area and flaky structure of GO for its function as a good support material [36]. Another additive, utilized for Acid Red 18 dye removal using Pal-nZVI is rGO due to its strong adsorbing properties. The long shelf life and the activity of the material over a wide range of pH is reported [19]. Zhang et al. reported sustained Fenton activity of GCN incorporated Pal-nZVI through regeneration of consumed Fe(0) from photo-generated electrons produced by GCN. In this study, palygorskite clay supported the process by enhancing the dispersion of nZVI [68].

3.3.3 Polymer Incorporated C-nZVI Materials

Polymers are special materials which can act as stabilizing agents for nZVI, Fenton reaction accelerators and adsorption enhancers. Studies have been conducted to integrate polymers such as polydopamine (PDA), polyethylene glycol (PEG), polyethersulfone (PES), carboxymethyl cellulose (CMC), carboxymethyl chitosan (CMCS) and polypyrrole (PPy) with clay materials to form polymer supported C-nZVI [61, 63, 64, 69].

Incorporation of PDA into C-nZVI has been reported to assist the remediation of Cr(IV) by Pal-nZVI owing to its role as an organic ligand which prevents the leaching of iron and its action as a redox mediator to facilitate the reduction of the contaminant. Moreover, PDA facilitates the reduction of Fe(III) to Fe(II) which further promotes the removal of oxyanions [64]. Chen et al. reported long-lasting Fenton activity of PPy incorporated Pal-nZVI due to the protection effect of PPy-Pal layers. The authors also observed short equilibrium times and high adsorption capacities for the removal of naphthol green B [63].

Eltaweil et al. observed excellent chelating and adsorption properties of CMCS incorporated Bent-nZVI. Depending on the operating pH, effective remediation of both cationic and anionic dyes was reported due to protonation of the amine group and deprotonation of carboxyl groups of CMCS. Furthermore, authors have mentioned the reusability of the material up to five cycles without significant loss of performance [69].

Another polymeric stabilizing agent used to enhance nZVI composites is PEG. According to the study carried out by Zhao et al. PEG incorporated Zeol-nZVI demonstrated restrained magnetic activity, higher reactivity, improved adsorption efficiency and a broad effective pH range [61]. Utilization of membranes for environmental remediation provides various advantages such as energy efficiency, chemical-free operation, perpetual separation, convenience of usage in hybrid processes and prominent expansion of capacity. Selvan et al. produced a Kaol-nZVI incorporated PES membrane for the efficient remediation of arsenite [70].

3.3.4 Mesoporous Material Incorporated C-nZVI Materials

Fusion of mesoporous materials and C-nZVI has also been studied. Improved adsorption capacity and hydrothermal stability have been observed in Zeol-nZVI by Guo et al. owing to the flexible pore structure and large specific surface area of incorporated MCM-41 [71].

3.4 C-nZVI Materials with Modified Clays

Li et al. have studied the degradation of 2,4-DCP using organo-Bent-nZVI. Three different organic compounds namely hexadecyl trimethyl ammonium chloride

(HTAC), octadecyl dimethyl benzyl ammonium chloride and aminocaproic acid have been used for the modification, out of which HTAC incorporated material possessed high inter-layer space and organophilic character. Due to this, increased adsorption of 2,4-DCP with subsequent Fenton oxidation was displayed which improved the contaminant degradation efficiency [35]. Usage of hexadecyl trimethyl ammonium chloride to enhance adsorption properties and performance of palygorskite was reported by Liu et al. [66].

Cetyltrimethylammonium bromide, a cationic surfactant, has been used to modify montmorillonite owing to its increased hydrophobicity and larger lamellar space. Compared with the pristine clay, organo modified materials portray superior adsorption capacities for organic contaminants. Organo-montmorillonite can also provide good mechanical support to nZVI [33].

An amino functionalized Verm-nZVI has been reported by Zhao et al. which could be easily protonated, promoting the remediation of anionic contaminants through feasible adsorption by electrostatic interactions and ion exchange mechanisms. Enhanced stability, considerate regeneration and reusability were also demonstrated by the material owing to the special properties of functionalized carrier [41].

4 Contaminant Remediation by C-nZVI Composites

Remediation activity of C-nZVI occurs due to the synergistic activity of both nanoparticle and clay [30]. This process can take place due to three possible mechanisms, (1) adsorption onto generated iron oxyhydroxides, (2) adsorption onto the binding sites of the carrier and (3) oxidative/ reductive degradation by nZVI [17]. Adsorption of an adsorbate onto clay surface can take place by electrostatic attraction owing to its surface negative charge. Furthermore, metallic contaminants can be coprecipitated on the clay surface after their reduction to the zero-valent state by nZVI [17].

4.1 Electron Transfer Mechanisms of nZVI

Oxidative and reductive electron transfer mechanisms of nZVI have been well documented [1, 11, 13]. As this chapter focuses extensively on the processes of C-nZVI remediation, the fundamentals of nZVI remedial mechanisms are provided in brief.

The oxidative transformation of organic contaminants by nZVI takes place through several approaches such as nZVI-induced Fenton reaction, free radical mediated AOPs and nZVI under aeration. Fenton reactions of nZVI are the most studied out of the three approaches. This mechanism is based on the extremely reactive hydroxyl and hydroperoxyl radicals generated from the reaction between hydrogen peroxide and Fe(0) [11]. The nZVI Fenton process is self-catalytic and depends on the oxidative dissolution of nZVI in the presence of hydrogen peroxide which acts as a scavenger of hydroxyl radicals. The pH for the reaction is provided by interfacial hydronium ions produced in-situ at the nZVI surface which enables continuous release of Fe(II) [1, 11].

Reductive transformation by nZVI is where Fe(0) is oxidized by contaminants which have a standard electrode potential greater than −0.44 V. In most cases, contaminants are transformed into more benign by-products as a result of the electron transfer. Electrons generated from the oxidation of nZVI can be used either to reduce contaminants or produce H_2 [11].

4.2 *Effect of pH*

The effect of pH on the remediation of contaminants has been discussed under organic molecules, heavy metals and oxyanions separately to provide clarity and ease of interpretation.

4.2.1 Effect of pH on Organic Molecule Remediation by C-nZVI Materials

The pH of the solution plays a pivotal role in the adsorption and Fenton activity of C-nZVI materials. In general, the degradation of organic contaminants is well favored and facilitated under acidic conditions and the rate of elimination decreases as pH increases [19, 30, 57, 60]. This can be attributed to several causes. Corrosion of iron in aqueous solution at low pH to form atomic and molecular hydrogen, hydronium ions and hydroxyl radicals is important for organic contaminant degradation [34, 60]. In addition, acidic conditions can dissolve the oxides and oxide coatings on the surface to Fe(II) in order to expose the iron core to accelerate redox reactions and Fenton activity [19, 30, 60]. At lower pH, the presence of oxonium ions in the organic contaminant will prevent the dissociation of surface acidic groups which enables the formation of H-bonds and π-π interactions with C-nZVI leading to maximum adsorption capacity [72].

However, strong acidic conditions can potentially decrease the rate and efficiency of organic contaminant degradation due to several special circumstances. (1) Rapid dissolution of nZVI in acidic medium at a rate faster than its self-catalysis leads to reduced Fenton activity, (2) formation of molecular hydrogen produces air bubbles on the catalyst which limits surface contact [73].

The decreased remediation of organic contaminants in alkaline medium has been attributed to a variety of reasons. Fe(II) has low solubility when alkalinity of the solution increases which leads to reduced Fenton activity [33]. In addition, rapid decomposition of hydrogen peroxide to oxygen and water, inhibition of hydroxyl radical generation and rapid scavenging of hydroxyl radicals by alkaline species would cause Fe(0) to react with hydroxyl ions to produce iron hydroxide at high pH causing a substantial decrease in contaminant degradation rates [30, 57]. Due to the deprotonation of surface silanol and aluminol groups on the clay substrate in aqueous alkaline media, a high negative charge is imparted onto the surface of the clay substrate which can repel several organic contaminants with electron donating moieties due to electrostatic repulsions [18].

4.2.2 Effect of pH on Heavy Metal Remediation by C-nZVI Materials

In general, heavy metals show maximum adsorption at mild acidic conditions [67, 74]. In contrast, strong acidic and alkaline conditions have been reported to be less favorable for sorption.

Heavy metals such as Cu(II) and Pb(II) can have alkaline precipitates preventing reductive remediation due to their low solubility products. But Ni(II) showed higher remediation as it has a solubility product higher by several magnitudes than that of Cu(II) which allows it to be more accessible in its soluble cationic form and have strong electrostatic interactions with the negatively charged surface of clay at neutral pH [59]. Another issue observed at alkaline pH is the formation of iron oxide layers which can block reactive sites diminishing adsorption [59, 74]. Furthermore, as mentioned in Sect. 4.2.1, decreased Fenton activity at high pH is another factor that contributes to diminished remediation.

In a strong acidic medium, the adsorption of heavy metals faces several challenges. An oxyhydroxide layer covering can form on the surface of cations decreasing adsorption [74]. In addition, sorption efficiency can get reduced due to competition posed by hydronium ions and excessive nZVI corrosion by the same [36, 67].

The point of zero charge (pH_{PZC}) plays an important role in the adsorption process. If the pH of the medium is higher than the pH_{PZC}, the surface becomes negatively charged due to deprotonation. This leads to higher electrostatic interactions with cationic species in their aqueous forms, leading to enhanced remediation [75]. Owing to the ion exchange process at the C-nZVI surface, there is high possibility of a significant reduction in pH during contaminant remediation.

A deviation from the general scheme is observed for Hg(II) which showed increased remediation at higher pH. The predominant species at alkaline conditions are observed to be mercury hydroxides which have higher mobility due to their smaller effective size when compared with the metal cation [75]. According to Kornilovych et al., charges of uranium species fluctuate based on different pH and maximum sorption are exhibited in a neutral pH range due to opposite charges of uranium ions and clay surface [53].

4.2.3 Effect of pH on Oxyanion Remediation by C-nZVI Materials

In contrast to metal cations, oxyanions require a positively charged surface for effective electrostatic interactions and adsorption that would lead to subsequent remediation. Therefore, oxyanion remediation is best observed when the pH of the medium is below the pH_{PZC} of C-nZVI [64]. As a result of the sensitivity of oxyanions to solution pH, adsorption under acidic conditions provided the best efficiency while the adsorption capacity reduced with increasing pH. Furthermore, higher protonation of nZVI and reduced surface passivation also occurs under acidic conditions leading to more remedial efficiency [31, 76].

At alkaline pH, a decrease in the removal capacity of C-nZVI can be seen as a result of hydroxyl ions competing for the same adsorption sites [77]. A strategy utilized to provide a wider pH range for the remediation of oxyanions is the introduction of protonated functional groups such as amino groups onto the C-nZVI material [41].

4.3 Kinetics of C-nZVI Associated Remediation

Some studies have reported adsorption kinetics for just the supporting substrate and then for the combined effect of both adsorption and redox degradation of the C-nZVI material. This enables the computation of redox-degradation kinetics of nZVI using the data obtained [18]. In these studies, it is understood that adsorption kinetics followed the pseudo-second order (PSO) model while degradation kinetics followed the pseudo first order (PFO) model. In contrast, a majority of reported studies have only focused on the kinetics of remediation by entire composite. All of these studies except for a few, report that the overall kinetics of remediation of the C-nZVI material is PSO. If the overall kinetics fit into a PSO model, the remediation might be adsorption dominated and if they fit a PFO model, the remediation might be redox degradation dominated. In addition, J. Suazo-Hernández et al. have reported that competition by other species in multi-component systems can adversely affect remediation kinetics [77]. The rate of contaminant remediation has been documented to be vastly increased in C-nZVI when compared to pristine nZVI.

4.4 C-nZVI Associated Free Radical Mediated AOPs

Remediation of organic contaminants and heavy metals via free radical mediated AOPs in persulfate (PS), peroxymonosulfate (PMS) and percarbonate (PC) media has been documented. Additional energy for heat or light and special equipment are not required when these systems are activated using Fe(II) [33].

4.4.1 Free Radical Mediated AOPs in Peroxymonosulfate and Persulfate Media

Ding et al. have synthesized Pal-nZVI for the immobilization of quinclorac in a PMS medium which supplied sulfate and hydroxyl radicals by the reduction of HSO_5^- with the use of Fe(0) present in the synthesized material. It also facilitated the reduction of Fe(III) to regenerate Fe(II) which in turn joined in the catalyzation of PMS to continuously produce hydroxyl radicals [58].

Under both aerobic and anaerobic conditions Fe(II) is generated by nZVI as shown in Eqs. (1) and (2). According to Eq. (3), PMS systems are activated by the generated Fe(II) to form hydroxy and sulfate radicals which readily react with the contaminants resulting in degradation and complete mineralization of the molecules.

Efficiency of activating the PS system is improved by nZVI, as it reduces the formed Fe(III) to Fe(II), which re-enters the activation process as per Eq. (4). Under anaerobic conditions Fe(III) forms from Fe(II) and that cation is subjected to hydrolysis to produce FeOOH which could react with the SO_4^{2-} ions (Eqs. 5, 6 and 7). This results in accumulation of intermediates such as oxides and sulfates on the reactive surface of the material. The activation of PMS system with nZVI to generate hydroxyl and sulfate radicals is shown in Eqs. (8), (9) and (10). Higher concentrations of nZVI leads to excessive production of Fe(II) which negatively affects the remediation process by scavenging the active radicals as per the Eqs. (11) and (12). With very high concentrations of PMS, undesirable reactions as in Eq. (13) will occur as a limitation to radical activity toward contaminant removal [58].

$$\text{Aerobic condition: } 2Fe^0 + 2H_2O + O_2 \rightarrow 2Fe^{2+} + 4OH^- \tag{1}$$

$$\text{Anaerobic condition: } Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{2}$$

$$Fe^{2+} + 2HSO_5^- \rightarrow Fe^{3+} + 2\dot{O}H + SO_4^{\cdot-} + SO_4^{2-} \tag{3}$$

$$Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+} \tag{4}$$

$$2Fe^{2+} + 2H_2O \rightarrow 2Fe^{3+} + 2OH^- + H_2 \tag{5}$$

$$Fe^{3+} + 2H_2O \rightarrow FeOOH + 3H^+ \tag{6}$$

$$FeOOH + SO_4^{2-} + H_2O \rightarrow FeSO_4 + 2OH^- + \frac{1}{2}H_2 + \frac{1}{2}O_2 \tag{7}$$

$$Fe^0 + HSO_5^- + 2H^+ \rightarrow Fe^{2+} + HSO_4^- + H_2O \tag{8}$$

$$HSO_5^- + Fe^{2+} \rightarrow Fe^{3+} + OH^- + SO_4^{\cdot-} \tag{9}$$

$$SO_4^{\cdot-} + H_2O \rightarrow \dot{O}H + H^+ + SO_4^{2-} \tag{10}$$

$$SO_4^{\cdot-} + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+} \tag{11}$$

$$\dot{O}H + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \tag{12}$$

$$SO_4^{\cdot -} + SO_4^{\cdot -} \rightarrow S_2O_8^{2-} \tag{13}$$

In a different study, Zhang et al. have observed a similar mechanism in the PS medium for the remediation of trichloroethylene (TCE) and Cr(IV) using Pal-nZVI [78]. Further, Wu et al. have utilized organo-Mont-nZVI in a PS medium to degrade sulfamethazine via sulfate and hydroxyl radicals formed by the reaction of $S_2O_8^{2-}$ with Fe(II) [33].

Under aerobic and anaerobic conditions Fe(II) is generated from nZVI as per Eqs. (14) and (15), respectively. In PS media, Fe(II) is produced by the reaction with persulfate ions as indicated in Eq. (16). Fe(0) also reacts with the formed Fe(III) to regenerate Fe(II) (Eq. 17). Initiation of sulfate radical generation through persulfate system activation is carried out by Fe(III) ions in accordance with Eq. (18). Alkaline conditions are not favorable for stable activation of PS medium, as there is a tendency of the formed free radicals to be quenched (Eq. 19). The same effect is seen at higher concentrations of PS, as it reduces the reactivity of available free radicals in the medium (Eqs. 20 and 21). In acidic media, Fe(II) is produced as per Eqs. (16) and (22) leading to sulfate radical generation demonstrated in Eq. (18). Even under acidic conditions, higher production of Fe(II) might lead to sulfate free radical scavenging. On the other hand, persulfate can also be decomposed as shown in Eqs. (23) and (24) to water and molecular oxygen in the presence of low pH conditions. Alkalinity favors the generation of hydroxyl radicals via the reaction with sulfate free radicals and water or hydroxyl ions according to Eqs. (25) and (26). This reduces the availability of sulfate free radicals for the contaminant remediation [33, 78].

$$Fe^{0} + H_2O + \frac{1}{2}O_2 \rightarrow Fe^{2+} + 2OH^{-} \tag{14}$$

$$Fe^{0} + 2H_2O \rightarrow Fe^{2+} + 2OH^{-} + H_2 \tag{15}$$

$$Fe^{0} + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} \tag{16}$$

$$Fe^{0} + 2Fe^{3+} \rightarrow 3Fe^{2+} \tag{17}$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{\cdot -} + SO_4^{2-} \tag{18}$$

$$Fe^{2+} + SO_4^{\cdot -} \rightarrow Fe^{3+} + SO_4^{2-} \tag{19}$$

$$SO_4^{\cdot -} + SO_4^{\cdot -} \rightarrow S_2O_8^{2-} \tag{20}$$

$$SO_4^{\cdot -} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\cdot -} \tag{21}$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{22}$$

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \tag{23}$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{24}$$

$$SO_4^{\cdot -} + H_2O \rightarrow SO_4^{2-} + \dot{O}H + H^+ \tag{25}$$

$$SO_4^{\cdot -} + OH^- \rightarrow SO_4^{2-} + \dot{O}H \tag{26}$$

4.4.2 Free Radical Mediated AOPs in Percarbonate Medium

In the presence of a PC medium which is a source of hydrogen peroxide, Danish et al. have studied the remediation of TCE using Ni(0) incorporated Zeol-nZVI composite. Fe(0) presents in the composite acted as the $2Na_2CO_3 \cdot 3H_2O_2$ activator to generate hydroxyl radicals which caused the degradation of TCE molecules [65].

In the aqueous medium, PC liberates hydrogen peroxide as seen in Eq. (27). At a low pH, Fe(0) is oxidized to Fe(II) (Eq. 28). Besides, Fe(II) is also generated via the electron transfer process from Fe(0) to peroxide in the acidic medium according to Eq. (29). Activation of PS system results in the formation of hydroxyl radicals by the generated Fe(II) and Fe(III) ions in consonance with Haber Weiss mechanism (Eq. 30). Simultaneous reduction of Fe(III) to Fe(II) takes place as seen in Eqs. (31) and (32). As suggested in Eqs. (33) and (34), higher concentrations of PC will reduce the reactivity of available free radicals in the medium via quenching. An additional catalytic metal can also take part in the activation of PC systems by accelerating the generation of hydroxy radicals according to the given reaction scheme (Eqs. 35 and 36). It will also participate in the regeneration of the consumed Fe(II) (Eq. 37).

$$2Na_2CO_3 \cdot 3H_2O_2 \rightarrow 2Na_2CO_3 + 3H_2O_2 \tag{27}$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{28}$$

$$H_2O_2 + Fe^0 + 2H^+ \rightarrow 2H_2O + Fe^{2+} \tag{29}$$

$$H_2O_2 + Fe^{2+} \rightarrow \dot{O}H + OH^- + Fe^{3+} \tag{30}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \dot{O}OH + H^+ \tag{31}$$

$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \tag{32}$$

$$H_2O_2 + \dot{O}H \rightarrow H_2O + \dot{O}OH \tag{33}$$

$$\dot{O}OH + \dot{O}H \rightarrow H_2O + O_2 \tag{34}$$

$$Ni^+ + H_2O_2 \rightarrow Ni^{2+} + \dot{O}H + OH^- \tag{35}$$

$$Ni^{2+} + H_2O_2 \rightarrow Ni^+ + \dot{O}OH + H^+ \tag{36}$$

$$Fe^{3+} + Ni^+ \rightarrow Fe^{2+} + Ni^{2+} \tag{37}$$

5 Limitations and Future Directions

As discussed in detail in this chapter, C-nZVI materials have been documented to be efficient and promising purifying methods for contaminated water. However, several challenges still exist for which solutions can be posed in the future studies. Suggestions are as follows.

Most reported work on C-nZVI target specific contaminants to evaluate their remediation efficiencies individually. Nevertheless, the performance of these nanocomposites can vary in competitive systems with other chemicals present. More studies should be conducted to understand the performance of C-nZVI in such environments. In addition, many studies have not been carried out in actual wastewater or natural water, spiked with known amounts of contaminants. This data is essential to survey the activity of other parties such as hydroxyl radical scavengers present in contaminated water which can cause drastic deviations from observed results.

Furthermore, almost all studies have been carried out on a laboratory scale. Large scale experiments need to be conducted as certain levels of activity which are feasible in laboratory conditions can fail at large scale. More research should be focused on studying the C-nZVI-based remediation of a wider range of organic contaminants including new persistent organic pollutants [79].

Current methods of C-nZVI preparation have been limited mostly to liquid phase reduction. Other methods of synthesis such as carbothermal reduction, ball milling processes and chemical vapor deposition can be explored [80]. There are only limited studies carried out to explain the sequence of C-nZVI composite formation and the C:nZVI ratios used. Therefore, more investigation is needed to get a thorough understanding of these aspects.

Further studies are needed to improve material shelf life and reusability. There are only a limited number of C-nZVI prepared using modified clays. Hence, research can be done to incorporate more novel modified clay into nZVI. In the recent past, novel eC-nZVI materials have been documented. However, there is potential for more composites of such nature with even better functionality. C-nZVI has better operating capabilities and working range than pristine nZVI but its remediation efficiency in neutral or alkaline conditions needs to be improved. Furthermore, to have a better understanding of the contribution made by the incorporated substance to the engineered material, performance of eC-nZVI should be compared with C-nZVI and each pristine component.

Most of the reported literature discuss kinetics of remediation for the entire C-nZVI material. However, some studies have discussed adsorption kinetics for the supporting material(s) without nZVI and then investigated the collective effect of adsorption and redox degradation by evaluating kinetics of the entire material. Thereafter, redox-degradation kinetics of nZVI have been computed. This approach is recommended for future studies as it provides a thorough understanding of the performance of pristine nZVI and support material.

Only a limited number of comparative studies have been carried out to evaluate the performance of C-nZVI with different clay minerals for a specific contaminant. Conducting more studies of this nature is important to get a thorough understanding of the performance of various types of C-nZVI.

6 Conclusions

There has been an increased focus on the use of C-nZVI for the treatment of many aquatic contaminants such as heavy metals, organic contaminants and oxyanions in the recent past. Inhibition of nanoparticle agglomeration and enhanced exposure of nZVI reactive sites in C-nZVI composites to contaminants directly result in better performance over pristine individual components. In alkaline conditions, the remediation of contaminants by C-nZVI is inefficient but attempts have been made to widen the operating pH range. In addition to sC-nZVI, the research focus for C-nZVI has been directed to produce eC-nZVI which have prolonged shelf life, sustained Fenton activity and improved adsorption characteristics. Free radical mediated AOPs have also attracted interest due to their enhanced electron transfer mechanisms. Many studies have demonstrated that C-nZVI composite materials hold significant promise for the purification of contaminated aqueous solutions. However, more comprehensive, systematic studies are required in the future research to understand the performance of C-nZVI in competitive systems, in wastewater and in the treatment of new persistent organic pollutants.

Acknowledgements Authors would like to acknowledge the financial support by the Institute of Chemistry Ceylon (Research grant no 21-2).

References

1. Ezzatahmadi, N., Ayoko, G.A., Millar, G.J., Speight, R., Yan, C., Li, J., Li, S., Zhu, J., Xi, Y.: Clay-supported nanoscale zero-valent iron composite materials for the remediation of contaminated aqueous solutions: a review. Chem. Eng. J. **312**, 336–350 (2017)
2. Peiris, C., Nawalage, S., Wewalwela, J.J., Gunatilake, S.R., Vithanage, M.: Biochar based sorptive remediation of steroidal estrogen contaminated aqueous systems: a critical review. Environ. Res. **191**, 110183 (2020)
3. Tesh, S.J., Scott, B.: Nano-composites for water remediation: a review. Adv. Mater. **26**(35), 6056–6068 (2014)
4. Ullah, S., Faiz, P., Leng, S.: Synthesis, mechanism, and performance assessment of zero-valent iron for metal-contaminated water remediation: a review. Clean - Soil Air Water **48**(9), 2000080 (2020)
5. Santhosh, C., Velmurugan, V., Jacob, G., Jeong, S.K., Grace, A.N., Bhatnagar, A.: Role of nanomaterials in water treatment applications: a review. Chem. Eng. J. **306**, 1116–1137 (2016)
6. Mukherjee, R., Kumar, R., Sinha, A., Lama, Y., Saha, A.K.: A review on synthesis, characterization, and applications of nano zero valent iron (nZVI) for environmental remediation. Crit. Rev. Environ. Sci. Technol. **46**(5), 443–466 (2016)
7. Zhao, X., Liu, W., Cai, Z., Han, B., Qian, T., Zhao, D.: An overview of preparation and applications of stabilized zero-valent iron nanoparticles for soil and groundwater remediation. Water Res. **100**, 245–266 (2016)
8. Samaraweera, H., Nawalage, S., Nayanathara, R.O., Peiris, C., Karunaratne, T.N., Gunatilake, S.R., Thirumalai, R.V., Zhang, J., Zhang, X., Mlsna, T.: In situ synthesis of zero-valent iron-decorated lignite carbon for aqueous heavy metal remediation. Processes **10**(8), 1659 (2022)
9. Sivodia, C., Sinha, A.: Clay supported zero valent iron nanocomposites: advancement in the field of green catalyst for abatement of persistent pollutant. In: New Trends in Emerging Environmental Contaminants, pp. 311–331, Springer (2022)
10. Lu, F., Astruc, D.: Nanocatalysts and other nanomaterials for water remediation from organic pollutants. Coord. Chem. Rev. **408**, 213180 (2020)
11. Phenrat, T., Le, T.S.T., Naknakorn, B., Lowry, G.V., Chemical reduction and oxidation of organic contaminants by nanoscale zerovalent iron (2019)
12. Li, Q., Chen, Z., Wang, H., Yang, H., Wen, T., Wang, S., Hu, B., Wang, X.: Removal of organic compounds by nanoscale zero-valent iron and its composites. Sci. Total Environ. **792**, 148546 (2021)
13. Puthukkara, A.R.P., Jose, S.T., Lal, D.S.: Plant mediated synthesis of zero valent iron nanoparticles and its application in water treatment. J. Environ. Chem. Eng. **9**(1) (2021)
14. Li, Y., Tian, G., Dong, G., Bai, S., Han, X., Liang, J., Meng, J., Zhang, H.: Research progress on the raw and modified montmorillonites as adsorbents for mycotoxins: a review. Appl. Clay Sci. **163**, 299–311 (2018)
15. Adusei-Gyamfi, J., Acha, V.: Carriers for nano zerovalent iron (nZVI): synthesis, application and efficiency. RSC Adv. **6**(93), 91025–91044 (2016)
16. Weerasooriyagedara, M., Ashiq, A., Gunatilake, S.R., Giannakoudakis, D.A., Vithanage, M.:Surface interactions of oxytetracycline on municipal solid waste-derived biochar–montmorillonite composite. Sustain. Environ. **8**(1) (2022)
17. Khandelwal, N., Tiwari, E., Singh, N., Darbha, G.K.: Heterogeneously porous multiadsorbent clay-biochar surface to support redox-sensitive nanoparticles: applications of novel Clay–Biochar–Nanoscale Zerovalent Iron Nanotrident (C-BC-nZVI) in continuous water filtration. ACS ES&T Water **1**(3), 641–652 (2021)

18. Baldermann, A., Kaufhold, S., Dohrmann, R., Baldermann, C., Letofsky-Papst, I., Dietzel, M.: A novel nZVI–bentonite nanocomposite to remove trichloroethene (TCE) from solution. Chemosphere **282**, 131018 (2021)
19. Xu, H., Tian, W., Zhang, Y., Tang, J., Zhao, Z., Chen, Y.: Reduced graphene oxide/attapulgite-supported nanoscale zero-valent iron removal of acid red 18 from aqueous solution. Water Air Soil Pollut. **229**(12), 1–16 (2018)
20. Zhang, T., Wang, W., Zhao, Y., Bai, H., Wen, T., Kang, S., Song, G., Song, S., Komarneni, S.: Removal of heavy metals and dyes by clay-based adsorbents: From natural clays to 1D and 2D nano-composites. Chem. Eng. J. **420**, 127574 (2021)
21. Khalid, M., Walvekar, R., Ketabchi, M.R., Siddiqui, H., Hoque, M.E.: Rubber/nanoclay composites: towards advanced functional materials. In: Nanoclay Reinforced Polymer Composites, pp. 209–224, Springer (2016)
22. Sethurajaperumal, A., Ravichandran, V., Banerjee, A., Manohar, A., Varrla, E.: Two-dimensional layered nanosheets: structure and unique properties. In: Fundamentals and Properties of Multifunctional Nanomaterials, pp. 465–497. Elsevier (2021)
23. Kumari, N., Mohan, C., Basics of clay minerals and their characteristic properties (2021)
24. Gu, C., Jia, H., Li, H., Teppen, B.J., Boyd, S.A.: Synthesis of highly reactive subnano-sized zero-valent iron using smectite clay templates. Environ. Sci. Technol. **44**(11), 4258–4263 (2010)
25. Zhou, C., Tong, D., Yu, W.:Smectite nanomaterials: preparation, properties, and functional applications. In: Nanomaterials from Clay Minerals, pp. 335–364. Elsevier (2019)
26. Nesse, W.D.: Introduction to Mineralogy. Oxford University Press, Oxford (2012)
27. Zhang, X., Lin, S., Chen, Z., Megharaj, M., Naidu, R.: Kaolinite-supported nanoscale zero-valent iron for removal of Pb2+ from aqueous solution: reactivity, characterization and mechanism. Water Res. **45**(11), 3481–3488 (2011)
28. Jia, H., Wang, C.: Comparative studies on montmorillonite-supported zero-valent iron nanoparticles produced by different methods: reactivity and stability. Environ. Technol. **34**(1), 25–33 (2013)
29. Uz-Zaman, K.A., Biswas, B., Rahman, M.M., Naidu, R.: Smectite-supported chain of iron nanoparticle beads for efficient clean-up of arsenate contaminated water. J. Hazard. Mater. **407**, 124396 (2021)
30. Bao, T., Damtie, M.M., Hosseinzadeh, A., Wei, W., Jin, J., Vo, H.N.P., Ye, J.S., Liu, Y., Wang, X.F., Yu, M.: Bentonite-supported nano zero-valent iron composite as a green catalyst for bisphenol a degradation: preparation, performance, and mechanism of action. J. Environ. Manag. **260**, 110105 (2020)
31. Yin, Y., Shen, C., Bi, X., Li, T.: Removal of hexavalent chromium from aqueous solution by fabricating novel heteroaggregates of montmorillonite microparticles with nanoscale zero-valent iron. Sci. Rep. **10**(1), 1–12 (2020)
32. Suazo-Hernández, J., Manquián-Cerda, K., de la Luz Mora, M., Molina-Roco, M., Rubio, M.A., Sarkar, B., Bolan, N., Arancibia-Miranda, N.: Efficient and selective removal of SeVI and AsV mixed contaminants from aqueous media by montmorillonite-nanoscale zero valent iron nanocomposite. J. Hazard. Mater. **403**, 123639 (2021)
33. Wu, J., Wang, B., Blaney, L., Peng, G., Chen, P., Cui, Y., Deng, S., Wang, Y., Huang, J., Yu, G.: Degradation of sulfamethazine by persulfate activated with organo-montmorillonite supported nano-zero valent iron. Chem. Eng. J. **361**, 99–108 (2019)
34. Weng, X., Cai, W., Lin, S., Chen, Z.: Degradation mechanism of amoxicillin using clay supported nanoscale zero-valent iron. Appl. Clay Sci. **147**, 137–142 (2017)
35. Li, G., Xu, Q., Jin, X., Li, R., Dharmarajan, R., Chen, Z.: Enhanced adsorption and Fenton oxidation of 2, 4-dichlorophenol in aqueous solution using organobentonite supported nZVI. Sep. Purif. Technol. **197**, 401–406 (2018)
36. Shao, J., Yu, X., Zhou, M., Cai, X., Yu, C.: Nanoscale zero-valent iron decorated on bentonite/graphene oxide for removal of copper ions from aqueous solution. Materials **11**(6), 945 (2018)
37. Weng, X., Sun, Q., Lin, S., Chen, Z., Megharaj, M., Naidu, R.: Enhancement of catalytic degradation of amoxicillin in aqueous solution using clay supported bimetallic Fe/Ni nanoparticles. Chemosphere **103**, 80–85 (2014)

38. Ye, J., Luo, Y., Sun, J., Shi, J.: Nanoscale zero-valent iron modified by bentonite with enhanced Cr (VI) removal efficiency, improved mobility, and reduced toxicity. Nanomaterials **11**(10), 2580 (2021)
39. Dada, A.O., Adekola, F.A., Odebunmi, E.O., Inyinbor, A.A., Akinyemi, B.A., Ilesanmi, D.A.: Kinetics and thermodynamics of adsorption of rhodamine B onto bentonite supported nanoscale zerovalent iron nanocomposite. In: Journal of Physics: Conference Series, IOP Publishing, p. 012106 (2019)
40. Wang, W., Wang, A.:Vermiculite nanomaterials: structure, properties, and potential applications. In: Nanomaterials from Clay Minerals, pp. 415–484, Elsevier (2019)
41. Zhao, R., Zhou, Z., Zhao, X., Jing, G.: Enhanced Cr (VI) removal from simulated electroplating rinse wastewater by amino-functionalized vermiculite-supported nanoscale zero-valent iron. Chemosphere **218**, 458–467 (2019)
42. Deng, H., Wu, Y., Shahzadi, I., Liu, R., Yi, Y., Li, D., Cao, S., Wang, C., Huang, J., Su, H.: Nanomaterials from mixed-layer clay minerals: structure, properties, and functional applications. In: Nanomaterials from Clay Minerals, pp. 365–413. Elsevier (2019).
43. Wang, F., Liu, D., Zheng, P., Ma, X.: Synthesis of rectorite/Fe3O4-CTAB composite for the removal of nitrate and phosphate from water. J. Ind. Eng. Chem. **41**, 165–174 (2016)
44. Olivier, J.P., Occelli, M.L.: Surface area and microporosity of pillared rectorite catalysts from a hybrid density functional theory method. Microporous Mesoporous Mater. **57**(3), 291–296 (2003)
45. Xiao, J., Peng, T., Ke, D., Zan, L., Peng, Z.: Synthesis, characterization of CdS/rectorite nanocomposites and its photocatalytic activity. Phys. Chem. Miner. **34**(4), 275–285 (2007)
46. Wang, W., Wang, A.:Palygorskite nanomaterials: structure, properties, and functional applications. In: Nanomaterials from Clay Minerals, pp. 21–133. Elsevier (2019)
47. Tian, G., Han, G., Wang, F., Liang, J.:Sepiolite nanomaterials: structure, properties and functional applications. In: Nanomaterials from Clay Minerals, pp. 135–201. Elsevier (2019)
48. Zhang, W., Qian, L., Ouyang, D., Chen, Y., Han, L., Chen, M.: Effective removal of Cr (VI) by attapulgite-supported nanoscale zero-valent iron from aqueous solution: enhanced adsorption and crystallization. Chemosphere **221**, 683–692 (2019)
49. Wang, D.-Y., Novel Fire Retardant Polymers and Composite Materials. Woodhead Publishing (2016)
50. Ainiwaer, M., Zeng, X., Yin, X., Wen, J., Su, S., Wang, Y., Zhang, Y., Zhang, T., Zhang, N.: Thermodynamics, kinetics, and mechanisms of the co-removal of arsenate and arsenite by sepiolite-supported nanoscale zero-valent iron in aqueous solution. Int. J. Environ. Res. Public Health **19**(18), 11401 (2022)
51. Wang, S., Peng, Y.: Natural zeolites as effective adsorbents in water and wastewater treatment. Chem. Eng. J. **156**(1), 11–24 (2010)
52. Mackenzie, K., Georgi, A.: NZVI synthesis and characterization. In: Nanoscale Zerovalent Iron Particles for Environmental Restoration, pp. 45–95. Springer (2019)
53. Kornilovych, B., Kovalchuk, I., Tobilko, V., Ubaldini, S.: Uranium removal from groundwater and wastewater using clay-supported nanoscale zero-valent iron. Metals **10**(11), 1421 (2020)
54. Soliemanzadeh, A., Fekri, M.: Synthesis of clay-supported nanoscale zero-valent iron using green tea extract for the removal of phosphorus from aqueous solutions. Chin. J. Chem. Eng. **25**(7), 924–930 (2017)
55. Gopal, G., Sankar, H., Natarajan, C., Mukherjee, A.: Tetracycline removal using green synthesized bimetallic nZVI-Cu and bentonite supported green nZVI-Cu nanocomposite: a comparative study. J. Environ. Manag. **254**, 109812 (2020)
56. Sravanthi, K., Ayodhya, D., Swamy, P.Y.: Green synthesis, characterization and catalytic activity of 4-nitrophenol reduction and formation of benzimidazoles using bentonite supported zero valent iron nanoparticles. Mater. Sci. Energy Technol. **2**(2), 298–307 (2019)
57. Rao, W., Lv, G., Wang, D., Liao, L.: Enhanced degradation of Rh 6G by zero valent iron loaded on two typical clay minerals with different structures under microwave irradiation. Front. Chem. **6**, 463 (2018)

58. Ding, C., Xiao, S., Lin, Y., Yu, P., Zhong, M.-E., Yang, L., Wang, H., Su, L., Liao, C., Zhou, Y.: Attapulgite-supported nano-Fe0/peroxymonsulfate for quinclorac removal: performance, mechanism and degradation pathway. Chem. Eng. J. **360**, 104–114 (2019)
59. Li, Z., Dong, H., Zhang, Y., Li, J., Li, Y.: Enhanced removal of Ni (II) by nanoscale zero valent iron supported on Na-saturated bentonite. J. Colloid Interface Sci. **497**, 43–49 (2017)
60. Ezzatahmadi, N., Millar, G.J., Ayoko, G.A., Zhu, J., Zhu, R., Liang, X., He, H., Xi, Y.: Degradation of 2, 4-dichlorophenol using palygorskite-supported bimetallic Fe/Ni nanocomposite as a heterogeneous catalyst. Appl. Clay Sci. **168**, 276–286 (2019)
61. Zhao, J., Yang, X., Liang, G., Wang, Z., Li, S., Wang, Z., Xie, X.: Effective removal of two fluoroquinolone antibiotics by PEG-4000 stabilized nanoscale zero-valent iron supported onto zeolite (PZ-NZVI). Sci. Total Environ. **710**, 136289 (2020)
62. Khandelwal, N., Tiwari, E., Singh, N., Marsac, R., Schäfer, T., Monikh, F.A., Darbha, G.K.: Impact of long-term storage of various redox-sensitive supported nanocomposites on their application in removal of dyes from wastewater: Mechanisms delineation through spectroscopic investigations. J. Hazard. Mater. **401**, 123375 (2021)
63. Chen, Y., Lin, Z., Hao, R., Xu, H., Huang, C.: Rapid adsorption and reductive degradation of Naphthol Green B from aqueous solution by Polypyrrole/Attapulgite composites supported nanoscale zero-valent iron. J. Hazard. Mater. **371**, 8–17 (2019)
64. Ma, B., Yao, J., Chen, Z., Liu, B., Kim, J., Zhao, C., Zhu, X., Mihucz, V.G., Minkina, T., Knudsen, T.Š: Superior elimination of Cr (VI) using polydopamine functionalized attapulgite supported nZVI composite: behavior and mechanism. Chemosphere **287**, 131970 (2022)
65. Danish, M., Gu, X., Lu, S., Brusseau, M.L., Ahmad, A., Naqvi, M., Farooq, U., Zaman, W.Q., Fu, X., Miao, Z.: An efficient catalytic degradation of trichloroethene in a percarbonate system catalyzed by ultra-fine heterogeneous zeolite supported zero valent iron-nickel bimetallic composite. Appl. Catal. A: Gen. **531**, 177–186 (2017)
66. Liu, Z., Yang, H., Wang, M., Sun, Y., Fei, Z., Chen, S., Luo, R., Hu, L., Gu, C.: Enhanced reductive debromination of decabromodiphenyl ether by organic-attapulgite supported Fe/Pd nanoparticles: Synergetic effect and mechanism. J. Colloid Interface Sci. **613**, 337–348 (2022)
67. Angaru, G.K.R., Choi, Y.-L., Lingamdinne, L.P., Choi, J.-S., Kim, D.-S., Koduru, J.R., Yang, J.-K., Chang, Y.-Y.: Facile synthesis of economical feasible fly ash–based zeolite–supported nano zerovalent iron and nickel bimetallic composite for the potential removal of heavy metals from industrial effluents. Chemosphere **267**, 128889 (2021)
68. Zhang, J., Zhang, T., Liang, X., Wang, Y., Shi, Y., Guan, W., Liu, D., Ma, X., Pang, J., Xie, X.: Efficient photocatalysis of CrVI and methylene blue by dispersive palygorskite-loaded zero-valent iron/carbon nitride. Appl. Clay Sci. **198**, 105817 (2020)
69. Eltaweil, A.S., El-Tawil, A.M., Abd El-Monaem, E.M., El-Subruiti, G.M.: Zero valent iron nanoparticle-loaded nanobentonite intercalated carboxymethyl chitosan for efficient removal of both anionic and cationic dyes. ACS Omega **6**(9), 6348–6360 (2021)
70. Selvan, B.K., Thiyagarajan, K., Das, S., Jaya, N., Jabasingh, S.A., Saravanan, P., Rajasimman, M., Vasseghian, Y.: Synthesis and characterization of nano zerovalent iron-kaolin clay (nZVI-Kaol) composite polyethersulfone (PES) membrane for the efficacious As2O3 removal from potable water samples. Chemosphere **288**, 132405 (2022)
71. Guo, Y., Huang, W., Chen, B., Zhao, Y., Liu, D., Sun, Y., Gong, B.: Removal of tetracycline from aqueous solution by MCM-41-zeolite a loaded nano zero valent iron: synthesis, characteristic, adsorption performance and mechanism. J. Hazard. Mater. **339**, 22–32 (2017)
72. Kadhum, S.T., Alkindi, G.Y., Albayati, T.M.: Eco friendly adsorbents for removal of phenol from aqueous solution employing nanoparticle zero-valent iron synthesized from modified green tea bio-waste and supported on silty clay. Chin. J. Chem. Eng. **36**, 19–28 (2021)
73. Han, X., Zhang, H., Zhang, C., Zhao, Y., Zhang, N., Liang, J.: Preparation of sepiolite nanofibers supported zero valent iron composite material for catalytic removal of tetracycline in aqueous solution. Front. Chem. 734 (2021)
74. Lakkaboyana, S.K., Khantong, S., Asmel, N.K., Obaidullah, S., Kumar, V., Kannan, K., Venkateswarlu, K., Yuzir, A., Yaacob, W.Z.W.: Indonesian Kaolin supported nZVI (IK-nZVI) used for the an efficient removal of Pb (II) from aqueous solutions: kinetics, thermodynamics and mechanism. J. Environ. Chem. Eng. **9**(6), 106483 (2021)

75. Sahu, M.K., Patel, R.K., Kurwadkar, S.: Mechanistic insight into the adsorption of mercury (II) on the surface of red mud supported nanoscale zero-valent iron composite. J. Contam. Hydrol. **246**, 103959 (2022)
76. Zhang, M., Yi, K., Zhang, X., Han, P., Liu, W., Tong, M.: Modification of zero valent iron nanoparticles by sodium alginate and bentonite: enhanced transport, effective hexavalent chromium removal and reduced bacterial toxicity. J. Hazard. Mater. **388**, 121822 (2020)
77. Suazo-Hernández, J., Sepúlveda, P., Manquián-Cerda, K., Ramírez-Tagle, R., Rubio, M.A., Bolan, N., Sarkar, B., Arancibia-Miranda, N.: Synthesis and characterization of zeolite-based composites functionalized with nanoscale zero-valent iron for removing arsenic in the presence of selenium from water. J. Hazard. Mater. **373**, 810–819 (2019)
78. Zhang, W., Qian, L., Han, L., Yang, L., Ouyang, D., Long, Y., Wei, Z., Dong, X., Liang, C., Li, J.: Synergistic roles of Fe (II) on simultaneous removal of hexavalent chromium and trichloroethylene by attapulgite-supported nanoscale zero-valent iron/persulfate system. Chem. Eng. J. **430**, 132841 (2022)
79. Sheriff, I., Debela, S.A., Mans-Davies, A.: The listing of new persistent organic pollutants in the stockholm convention: its burden on developing countries. Environ. Sci. Policy **130**, 9–15 (2022)
80. Pasinszki, T., Krebsz, M.: Synthesis and application of zero-valent iron nanoparticles in water treatment, environmental remediation, catalysis, and their biological effects. Nanomaterials **10**(5), 917 (2020)

Silver Applied Ceramic Filters as Point-of-Use Water Treatment Device

Joshua Nosa Edokpayi, Mukhethwa P. Mannzhi, Musiwa P. Sadiki, and Nduvho M. Tshidumo

Abstract The sustainable access to clean and safe water has resulted to improved health outcomes. Millions of deaths of underage children have been linked to the consumption of microbial contaminated water from various sources. The cost of the provision of centralized water infrastructure for potable water supply is high and becoming unbearable for many developing countries across the globe. The invention of several point-of-use water treatment devices has aided the provision of safe water for human consumption at the household level. One of such water treatment devices is the use of silver-impregnated ceramic water filters. The material used are often of local origin which makes it cheap and affordable for many. This chapter report on the use of various forms of silver-applied ceramic filters, the mode of silver application as well as the socioeconomic factors that favors its use under different settings.

Keywords Ceramic water filter · Silver nanoparticles · Water quality · Human health · Point-of-use water treatment technology

1 Introduction

The availability and accessibility of clean and safe water for human consumption is a critical issue around the world, hence the need for cheap and effective ways of treating water. Low-income communities mostly face the burden caused by water-related illnesses and the high demise rate of young children [82]. According to the World Health Organization (WHO), the highest number of deaths related to waterborne diseases have been estimated to be due to the consumption of microbial contaminated water [86, 85]. Furthermore, water-related diseases can lead to chronic diarrhea caused by a bacterial infection linked to the consumption of food and water that have been defiled by feces [44, 82]. The consumption of such water hampers a child's development at the time of infection and could affect them cognitively in the

---

J. N. Edokpayi (✉) · M. P. Mannzhi · M. P. Sadiki · N. M. Tshidumo
Water and Environmental Management Research Group, Faculty of Science, Engineering and Agriculture, University of Venda, Private Bag X5050, Thohoyandou 0950, South Africa
e-mail: Joshua.Edokpayi@univen.ac.za

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_22

future. Despite the progress that has been made on sustainable access to safe drinking water as at 2022, about 2 billion people still consume microbial contaminated water [87].

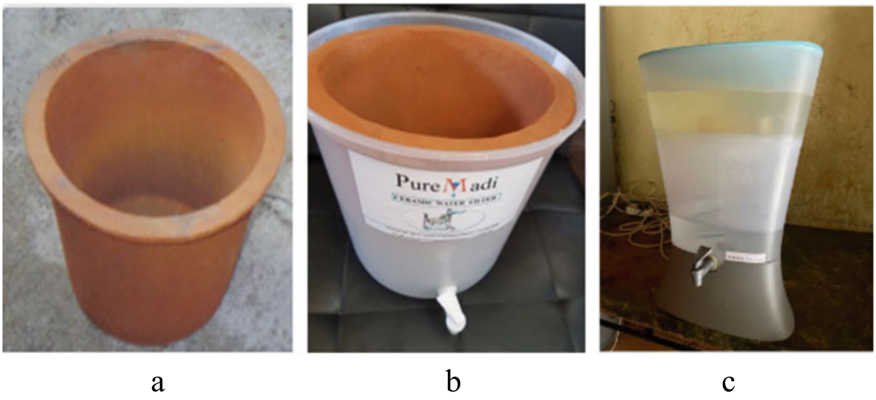
In many low-income countries, access to safe water and sanitation has been reported to be low, and rural communities rely on flowing streams which are profoundly turbid [23, 26]. Although water from water supply infrastructure is monitored for quality, many households still face water shortages and poor water quality, and this is partly because the municipal water distribution systems are not always maintained properly leading to a great amount of water loss and ingress of water contaminants. Residents of most of the affected areas are compelled to rely on polluted water for drinking, and this results in waterborne diseases [28, 4]. The erratic supply of potable water has encouraged the use of alternative sources of drinking water such as rivers, lakes, streams, non-protected springs, wetlands, ponds, harvested rainwater, and groundwater [2, 20, 44]. However, most of these water sources are majorly polluted by communities living near them (with several domestic activities such as laundry, agriculture including animal watering, deposition of solid waste amongst others), and from non-point sources of pollution [20]. Therefore, it is highly crucial to have access to clean and safe water to support public social welfare and development [5].

Furthermore, many regions of low-income countries do not have a centralized water purification system for the supply of clean and safe water; this is either due to the terrain of such places or the lack of adequate funds to run an effective water treatment and supply system. The use of other alternatives for water treatment becomes the most viable option [35]. The World Health Organization (WHO) has proposed the use of a decentralized approach of water treatment at the point of use in households, and this is commonly known as point-of-use water treatment technologies (POUWTTs) [75]. The POUWTTs have been widely used as a more practical treatment option due to their potential in improving the quality of water at the point of consumption. POUWTT provides an inexpensive and effective solution to decrease waterborne diseases by aiding families to treat water in their households before drinking, thus minimizing the gamble of recontamination, which can occur during transport and storage [32]. The major problem associated with the use and consumption of the various drinking water alternatives has to do with turbidity and microbial contamination. Although chemical contamination has been reported, the influence of poor microbial quality remains the major focus of most POUWTTs [52].

Currently, there are different promising point-of-use water treatment (POUWT) methods widely used such as biosand filters [89], chlorine tablet [45], ceramic water filters (CWF) [48], sunlight disinfection [15], the use of activated carbon [8], ceramic tablet [57], Madidrop [33], and aqua salveo [7]. Most of these methods have been applied successfully in laboratories, their performance in the community setting can vary depending on various factors, such as the ease of use, acceptability, and user compliance can affect their effectiveness when used in households [5, 21]. This study reports on CWF which uses silver in various forms as a disinfectant to improve microbial inactivation. Ceramic water filter is among the most practical and sustainable technology for water treatment at the household level which have low maintenance cost, highly affordable, easy to use, effective in bacterial inactivation, and reduces turbidity in water [88].

2 Ceramic Water Filters (CWFs) Production

CWFs are a type of POUWTTs (Fig. 1) used in rural communities that do not have access to centralized drinking water treatment systems [13]. CWFs have been widely regarded as one of the best water treatment innovation for household drinking water and have been produced by various organizations such as Potters for Peace (United states of America), PureMadi company (South Africa), Ceramic Water Purifier (Cambodia), Chijuo water filters (Kenya), NGO Thirst-Aid (Thailand), Colloidal silver filter (Nepal) to help with decreasing the problem of drinking contaminated water in developing countries and during emergency caused by natural disaster such as earthquakes, hurricanes and during wars to provide displaced people with clean and safe water [46, 54]. According to to Lemons et al. [41], ceramic filters are a socially acceptable alternative for drinking water treatment as they are easy to use, cheap, locally available, and do not introduce any smell or taste to the water. The filters are known to be easy to produce in most developing countries for intended use, as it is known to be comprised of a mixture of clay and burnout materials like sawdust, which is then followed by molding into shape, drying, and firing at a controlled temperature [82]. There are several stages involved in the production of CWF shown in Fig. 2. Although some of the stages can be modified by each of the CWF manufacturers to suit their needs.



a b c

Fig. 1 Various CWF used **a** The Potters for Peace filter [40]; **b** PureMadi water filter [65] and **c** Kohler clarity filter

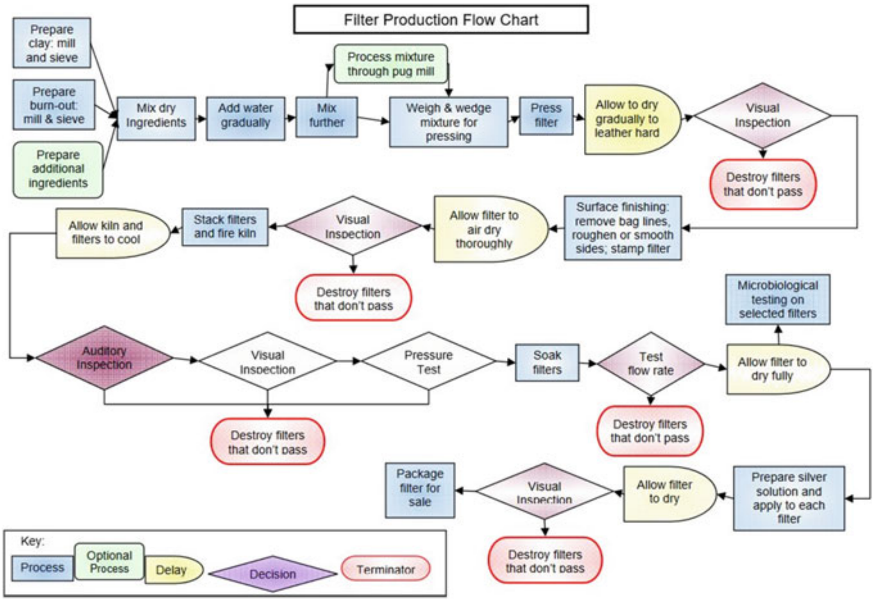


Fig. 2 Filter production chart (*Source* https://wiki.lowtechlab.org/wiki/Filtre_à_eau_céramique/en)

Table 1 shows some of the major factors to be considered during CWF production. One of the major ingredients used in ceramic water filter production is the clay material; however, the clay materials are different in mineralogical constituents. The three major clay groups which are Montmorillonite, Illite, and Kaolinite have been reportedly used in the manufacture of CWFs but the most widely reported is that of Kaolinite clays. Most of the clay materials used for CWF production were selected because of their availability, low cost, and less energy required during the production of the filters. Materials such as sawdust, grog, and rice husks are usually used to aid the porosity of the filter, but sawdust has been widely reported than others [55, 30]. Some CWF producers also add activated carbon and charcoal as additional components to aid the efficiencies of the filters.

The firing temperature used for CWF production varies depending on the kind of clay material used and the type of the furnace used [25]. Several kinds of kiln have also been reported ranging from the traditional and homemade kilns to the clamp kilns. Different fuel types have been reported for heating the kilns such as fuelwood, dried twigs, and cow dungs [14, 30]. Some CWF factory like the Pure Madi uses an electric furnace.

After firing, some common test are routinely performed on the filters and this include: pressure test, flow rate test, microbial removal efficiency test, and turbidity reduction test. This is done to verify its suitability before distribution [4]. During the filter production after firing some CWF producers do not add silver before distribution, while others add silver via painting in form of silver nanoparticles and silver nitrate solution although some uses silver nitrate salt prior to firing.

Table 1 Materials used for ceramic filter production

Burn-out materials	Nature of silver used	Furnace temperature (°C) & time	Mass of clay per filter (kg)	Country	Reference
Rice husk	None	900 for 2 h	0.24	Benin Republic	Akowanou et al. [3]
Sawdust	None	Temp N/R run for 1 h	2.75	North-eastern, Zimbabwe	Chaukura et al. [14]
Sawdust	None	850 and 950	N/R	Nigeria	Ekpunobi et al. [23]
Sawdust and grog[a]	Silver nitrate and silver nanoparticles	950 for 8–12 h	2	South Africa	Ndebele et al. [56]
Sawdust	Silver nitrate	900–1400 for 4 h	N/R	Vietnam	Dung et al. [19]
Sawdust	Silver nanoparticles	877–1006	N/R	Nigeria	Akosile et al. [4]
Rice husk	None	950–990 for 8–9 h	N/R	Haiti	Guerrero-Latorre [30]
Sawdust and grog	None	700, 750 and 800	N/R	Southern Ethiopia	Bulta and Michael [12]
Sawdust	Silver nitrate and Silver nanoparticle	900 for 3 h	0.17	Earysville, Virginia (USA)	Jackson and Smith [35]

Grog[a]–a filter that filter did not pass the test can be re-used as a burnout material. N/R–Not reported. The most common clay type was kaolinite although for some studies the kind of clay used was not reported.

3 Kind of Silver Used in CWF Production

Sustainable access to clean and safe water is a fundamental human need [56]. Although the use of CWF without the addition of a disinfectant has recorded about 2 log reduction of *E. coli*, reports from previous studies have shown that the addition of silver in its various forms has aided the pathogen inactivation potential of CWFs [37]. Silver has been widely used in CWFs in a variety of ways. According to [56], silver nanoparticles are the primary antimicrobial agent that is commonly added to CWF to help with inactivation of microorganisms, reduce the transmission of pathogens in treated water, and hinder the growth of biofilms on the surface of the filters.

The use of silver nitrate as an alternative to silver nanoparticles is constantly being tested due to potential workplace inhalation exposure risks and the high cost associated with the use of AgNPs [35]. The effectiveness of ceramic water filters with added silver nitrate for the reduction of *E. coli* was examined by [37] in Indonesia, and the findings revealed that ceramic water filters significantly reduces the levels of *E. coli*. The adoption $AgNO_3$ in the manufacture of ceramic filters could potentially enhance microbiological performance, lower production costs, improve the safety and occupational health of the CWF manufacturers, as well as improve consumer safety when using ceramic water filters for household water treatment [56].

4 Method of Silver Application on CWF

Silver nitrate and silver nanoparticles have been added to CWF using various modes such as painting, mixing before firing, and dipping.

Painting method: The porous ceramic filter is painted with AgNPs on both the interior and the exterior after firing (Fig. 3). Contaminated drinking water will receive long-term water disinfection due to the silver that adhere to the ceramic filter's pores [56]. Similarly, $AgNO_3$ solution has been painted to ceramic filter and ceramic disk for water disinfection in different concentration range. Varying levels of silver retention have been reported as well as the levels in the treated water. Most CWF and disk produced using this method conformed to the EPA standard of 100 ppb in the treated water. Although the characteristic of the raw water and the kind of clay materials used in the filter production plays a major role in the leaching of silver from the ceramic filter material which might affect the lifespan of the filter. It has been reported that AgNPs have higher retention on CWF than $AgNO_3$ solution if the painting method is employed after the filter production [49].

However, there are several limitations associated with the painting of CWFs with AgNPs. Silver nanoparticles are imported by many filter manufacturing facilities, mostly in the developing world as they are not locally available in the market, and this influences the cost of the final product. However, there can be leaching of ionic silver, especially in the early stages of the filter use; this could result in silver concentrations in the treated water exceeding 100 ppb, the threshold level of the regulatory standard [84]. The inhaling of silver nanoparticles during painting may have genotoxic effects; therefore, using AgNPs during the manufacturing process may put the health of those producing the filters at risk [27, 35], but this can easily be offset if proper personal protective equipment are used.

Dipping method: The way the silver is put into the filter has an impact on both how much silver is released and how well the filter works. Silver has been applied on CWFs also by dipping [73]. The pressure generated during dipping drives the silver particles into the pores of the ceramic when CWFs are dipped into a solution of AgNPs. In this production setting, the silver tends to concentrate on the exposed surfaces close to the pores. With dip coating, little to no silver is imbedded on the ceramic's interior [72].

Mixing before firing method: This is a common method associated with the use of $AgNO_3$ in CWF. The $AgNO_3$ solution is added at an appropriate level to create the desired ionic silver levels in the filters before firing [36, 56]. Hence, $AgNO_3$ is added as part of the raw materials needed to make the silver. This method reduces a stage of

Fig. 3 Application of aqueous silver nanoparticles [65]

the CWF production when compared with the dipping and painting methods with the disadvantages associated with them. Filters with fired-in $AgNO_3$ need between 5 to 10 times as much silver as filters with painted AgNPs to have the same log reduction values (LRVs), and $AgNO_3$ is more than 10 × cheaper when compared to AgNPs. A similar quantity of silver is released during dipping and painting,however, about 0.3% is released when mixed before firing [68]. Therefore, there is a higher silver retention using this method compared to other known methods [35]. The drawback to this method is the potential loss of silver if the CWF fails the performance tests such as the flow rate and pressure test.

5 The Efficiency of CWF Against Bacteria, Viruses, and Protozoans

Viruses, bacteria, and protozoa are simply transmitted by consuming contaminated water. Ingestion of these microorganisms in water poses one of the greatest health concerns resulting in waterborne illnesses [86]. The effectiveness of a CWF is frequently evaluated by how well it can destroy a variety of water pathogens. Many bacterial and protozoans can be effectively removed by most ceramic filters, while some tiny viral species cannot be inactivated [70, 72, 80].

5.1 The Efficiency of CWFs Against Bacteria

CWFs have demonstrated efficacy against a variety of pollutants, including bacteria [40, 73, 37] revealed that ceramic filters coated in silver nitrate and made of clay and bran (with compositions of 80 and 20%) may completely exclude *E. coli* from water. Table 2 below summarizes the effectiveness of ceramic filter against bacteria.

5.2 The Efficiency of CWF Against Viruses

According to Coleman et al. [17], viruses are responsible for about 1.3 million deaths annually due to diarrheal disease morbidity and mortality. It has been determined that viruses are a substantial factor in the global burden of diarrheal illness morbidity

Table 2 Effectiveness of CWF against some microbial indicator organisms

Bacterial type	Reduction %	LRV (lo g_{10})	Reference
Total coliform *E. coli*	94.70 99.40	NR NR	Ndebele et al. [56]
Total coliform *E. coli*	88.67 99.50	4.06–4.11 3.85–3.92	Jackson and Smith [35]
E. coli *Enterococus faecalis*	NR NR	> 6.00 > 3.00	Dankovich and Gray[18]
Ccryptosporidium parvum *E. coli*	NR 98.00	4.30 NR	Lantagne [40]
Escherichia coli *Clostridium spores*	NR NR	3.00–6.80 3.30–4.90	Clasen and Boisson [16]
E. coli	99.34	NR	Kendarto et al. [37]
Escherichia coli *Bacteriophages* MS2	99.00 90.00–99.00	2.10–2.90 1.20–4.10	Brown and Sobsey [11]

[a] NR- Not reported

and mortality, with the rotavirus alone accounting for 199,000 fatalities in 2015 [31, 38]. Excellent log reduction values (LRVs) are produced by CWF for bacterial and protozoan infections, but very little viral elimination is achieved [45]. The efficiency of virus elimination remains a serious challenge for ceramic water filters technology.

According to prior studies, utilizing ceramic water filters can marginally reduce the number of viruses present. Lantagne (2001) reported that colloidal silver-impregnated ceramic filters resulted in a 0.09–0.5log10 reduction for MS2 virus which is quite low. In Nicaragua, Ghana, and Cambodia, [81], reported that typical MS2 reductions for ceramic filters with silver modifications varied from 0.5 to 1log10 after 5 weeks and from 1 to 2 log10 after 13 weeks of use. For the best level of virus protection, a 3 LRV or above is recommended by the WHO guideline for domestic water treatment and safe storage methods. Although [76] reported that CWF can achieve a virus inactivation in the range of 0.5 to 4log10, the majority of cases reported show poor virus inactivation. This is currently one of the drawbacks to the use of CWF as POUWTT. However, it has been proven that there is a synergistic effect against viruses if silver and copper are used together. This presents a research gap in the CWF production that can be explored and tested both in the laboratory and under real settings. The success of this will lead to a transformation in the production and use of CWF [22, 77].

5.3 The Efficiency of CWF Against Protozoa

Water treatment systems intended to provide potable drinking water must continuously meet a 6log10 decrease in bacteria, a 4log10 reduction in viruses, and a 3log10 reduction in protozoa, as stated by the National Sanitation Foundation and the United States Environmental Protection Agency [79]. The study by Mona [45] and [17] reported that CWF usage in the laboratory and the field reduced the risk of waterborne illness by a factor of three with a high percentage of protozoa removal from water. Prior investigations on protozoa and protozoan surrogates showed high removal rates (>4log10) by CWF for protozoa such as *Giardia lambia* and *Cryptosporidium parvum*, as well as a 3.3–4.9 log10 removal of protozoan surrogate *C. perfringens* [81].

6 Other Water Quality Improvement

Point-of-use (POU) water treatment methods, which enhance the quality of drinking water at the household level, provide an inexpensive and practical option to acquire safe drinking water and hence can help prevent waterborne disease outbreaks [88]. The use of silver-impregnated ceramic filter was reported to lower the turbidity of muddy water from 950 to 0.45 NTU in the study conducted by Issa et al. [34]. Abebe et al. [1] also recorded the removal of turbidity from an initial value in the range

Table 3 Water hardness agents removal efficiency [12]

	Initial concentration before filtration (ppm)	Final concentration range after filtration (ppm)	Percentage (%) removal range efficiency
Ca^{2+}	56.25	13.87–39.00	30.10–75.30
Mg^{2+}	19.75	4.60–13.00	34.18–76.71
$SO_4{}^{2-}$	46.00	1.50–12.00	73.90–96.70
$PO_4{}^{3-}$	5.40	0.50–2.60	51.90–90.70

of 9.7−13.1 NTU in the unfiltered water to a range of 0.1 to 0.5 NTU of filtered water which is below the WHO recommended value of 1 NTU. Maciel et al. [43] reported a turbidity reduction ranged from 30 to 93%. However, the long-time use of CWF for highly turbid water may have a negative impact on the lifespan and water purification efficiency of ceramic water filters [62].

Ceramic filters have been demonstrated by Bulta and Micheal [12] to have outstanding reduction efficiency for Mg^{2+} and Ca^{2+} (Table 3). Additionally, Bulta and Michael [12] demonstrated that turbidity (59.6%), iron (52.88%), calcium (56.9%), phosphate (76.2%), magnesium (59.02%), sulfate (88.98%), and nitrite (46.23%) were all averagely removed by ceramic filters.

7 Health Improvements Reported Using CWF

The prevalence of diarrhea among children under the age of 5 was reduced after the use of CWF [61]. Williams [83] conducted a study in a rural (Namasagali) and an urban (Kampala) community in Uganda, and of the 52 cases of diarrhea reported prior to the distribution of CWFs (with $AgNO_3$) to 185 households, after three months of the study only four cases of diarrhea incidents were reported. CWFs used in Bolivia, South America served as a solution to diarrhea problem providing clean water to citizens. Zero levels of fecal coliforms were recorded in the effluent of the filters and diarrhea cases decreased by 70 and 83% in adults and children under the age of five, respectively [29]. The use of CWF as POUWTT has led to a huge decrease of water-related diseases in Makwane communities in South Africa that do not have access to treated water supply [53].

An improvement in the health and well-being of water users such as breadwinners, children, and elderly has been linked with the use of CWF at household level since they are preserved from drinking contaminated water with the associated health risk [63, 71]. In another study conducted in Kassala State (Sudan), CWFs were used to treat water with the purpose of reducing diarrhea in 1152 children under the age of 6, and it was successful. Although waterborne diseases were reduced with the use of CWF, there is however, no direct link with weight improvement or prevention of stunting. The study of Okotch et al. [60] in Sudan did not record a significant difference in the weight of children who uses CWF and those that do not. Similarly, Hill et al. [33] also did not record a significant height and weight improvement in children below the age of 3 drawn from 404 households in South Africa that uses CWF from the control group.

8 Cost of CWF and Acceptability

The price of the material used during the production of any device influences the cost of the final product. Moraes et al. [51] reported that CWF production cost determines the selling price. This selling price includes production cost, profit, marketing, and administration expenses [58]. Table 4 displays price lists of CWF in different countries. The conversion rate used was the US dollar rate of September 2022. End users of CWF prefer filters that perform better and still affordable,however, some CWF prices exceeds the income of some people in low-income settings who are living in poverty [67]. Many households that received CWFs during a field study recommended it as being useful, however, some cannot afford it.

CWF has been accepted by many households as a POUWTT which can be dependable, with no energy or chemical requirement, easy to use, move, and clean when clogged [42, 53, 77]. Moreover, the improvement of water turbidity increased its acceptability as water from most sources can be used [24, 60]. However, over time, the flow rate of the CWF reduces due to the pores being clogged and this can easily be removed by scrubbing the water receptacle of the filter, this may reduce the lifespan of the filters if highly turbid water is used most of the time [82], but its lifespan is reasonable compared to the initial investment. With proper maintenance adhering to

Table 4 Various costs of ceramic water filters

Location/country	Price (USD)	Reference
Btikk, Indonesia	3.26	Normal [58]
Hobeni village, South Africa	31.60	Lange et al. [39]
Dehli, India	14.00	Meierhofer et al. [47]
Cali, Colombia	76.62	Rivera-Sánchez et al. [71]
Kampala, Uganda	22.60	UNICEF [78]
Kandal, Cambodia	10.00	Brown and Sobsey [11]
Hamaskraal, South Africa	22.06	Ndebele et al. [56]
Stefani, Brazil	164.99	Amazon [6]
Phnom Penh, Cambodia	20.00	RDIC [69]
Colombia, Canada	25.00	PWB [64]

the instructions in the user's manual, it has been discovered that CWF can last up to 5 years [88]. Other factors apart from cost the influences end-users choice of the kind of CWF to be used include, the color, taste, and odor of the treated water [24].

9 Conclusion

Sustainable access to portable water remains a global challenge that may not end anytime soon. The means of purifying water at the point-of-use seems to be an alternative solution to improve drinking water quality since municipalities and local governments are struggling to supply potable water to households. CWF technology has been designed, used and accepted to be effective as a POU water treatment technology. Scientific reports of effective removal of bacteria, protozoans and turbidity improvement from raw water are impressive. Future studies should look at the innovation of CWF in removing viruses and other hazardous chemicals from drinking water sources.

References

1. Abebe, L.S., Smith, J.A., Narkiewicz, S., Oyanedel-Craver, V., Conaway, M., Singo, A., Amidou, S., Mojapelo, P., Brant, J., Dillingham, R.: Ceramic water filters impregnated with silver nanoparticles as a point-of-use water-treatment intervention for HIV-positive individuals in Limpopo Province, South Africa: A pilot study of technological performance and human health benefits. J. Water Health **12**(2), 288–300 (2016)
2. Adeeyo, A.O., Ndlovu, S.S., Ngwagwe, L.M., Mudau, M., Alabi, M.A., Edokpayi, J.N.: Wetland resources in South Africa: threats and metadata study. Resources **2022**(11), 54 (2022). https://doi.org/10.3390/resources11060054
3. Akowanou, A.V.O., Deguenon, H.E.J., Groendijk, L., Aina, M.P., Yao, B.K., Drogui, P.: 3D-printed clay-based ceramic water filters for point-of-use water treatment applications. Prog. Addit. Manuf. **4**(3), 315–321 (2019)
4. Akosile, S.I., Ajibade, F.O., Lasisi, K.H., Ajibade, T.F., Adewumi, J.R., Babatola, J.O., Oguntuase, A.M.: Performance evaluation of locally produced ceramic filters for household water treatment in Nigeria. Scientific African **7**, 1–13 (2020)
5. Aliyu, A., Usman, M., Audu, N.: Development of ceramic disc water filter for domestic use. Development **17**(5), 176–189 (2019)
6. Amazon.: Stéfani São João Brazilian clay water filter (10 L—2.6 gal), Brown (2022). https://www.amazon.com/S%C3%A3o-Jo%C3%A3o-St%C3%A9fani-BrazilianFilter/dp/B07NWRVRQZ?th=1. Accessed 11 Oct 2022
7. Amoah, A., Asiama, R.K., Korle, K., Kwablah, E.: Domestic water improvement behaviour: The probability determinants and policy implications. Water Policy **23**(4), 880–896 (2021)
8. Bari, M.N., Khatun, M.S, Fatema Khatun, H.R.: Removal of colour from wastewater using locally available charcoal. In 2nd International conference on civil engineering for sustainable development. Pp 14–16(2014)
9. Boisson, S., Stevenson, M., Shapiro, L., Kumar, V., Singh, L.P., Ward, D., Clasen, T.: Effect of household-based drinking water chlorination on diarrhoea among children under five in Orissa, India: a double-blind randomised placebo-controlled trial. PLoS Med. **10**(8), 1–12 (2013)

10. Brown, J., Sobsey, M.D., Loomis, D.: Local drinking water filters reduce diarrheal disease in Cambodia: A randomized, controlled trial of the ceramic water purifier. Am. J. Trop. Med. Hyg. **79**, 394–400 (2008)
11. Brown, J., Sobsey, M.D.: Microbiological effectiveness of locally produced ceramic filters for drinking water treatment in Cambodia. J. Water Health **8**, 1–10 (2010)
12. Bulta, A.L., Micheal, G.A.W.: Evaluation of the efficiency of ceramic filters for water treatment in Kambata Tabaro zone, southern Ethiopia. Environ. Syst. Res. **8**, 1–15 (2019)
13. Ceramics Manufacturing Working Group (CMWG).: Best practice recommendations for local manufacturing of ceramic pot filters for household water treatment. The Ceramics Manufacturing Working Group: Atlanta, Georgia, United State of America (2011)
14. Chaukura, N., Chiworeso, R., Gwenzi, W., Motsa, M.M., Munzeiwa, W., Moyo, W., Chikurunhe, I., Nkambule, T.T.: A new generation low-cost biochar-clay composite 'biscuit'ceramic filter for point-of-use water treatment. Appl. Clay Sci. **185**, 1–10 (2020)
15. Chaúque, B.J.M., Rott, M.B.: Solar disinfection (SODIS) technologies as alternative for large-scale public drinking water supply: Advances and challenges. Chemosphere **281**, 1–19 (2021)
16. Clasen, T., Boisson, S.: Household-based ceramic water filters for the treatment of drinking water in disaster response: An assessment of a pilot programme in the dominican republic. Water Pract. Technol., **1**, (2006)
17. Coleman, C.K., Mai, E., Miller, M., Sharma, S., Williamson, C., Oza, H., Holmes, E., Lamer, M., Ly, C., Stewart, J., Sobsey, M.D., Abebe, L.S.: Chitosan coagulation pretreatment to enhance ceramic water filtration for household water treatment. Int. J. Mol. Sci. **22**(18), 1–17 (2021)
18. Dankovich, T.A., Gray, D.G.: Bactericidal paper impregnated with silver nanoparticles for point-of-use water treatment. Environ. Sci. Technol. **45**, 1992–1998 (2011)
19. Dung, T.T.N., Thi, L.A.P., Nam, V.N., Nhan, T.T., Quang, D.V.: Preparation of silver nanoparticle-containing ceramic filter by in-situ reduction and application for water disinfection. J. Environ. Chem. Eng. **7**(3), 1–10 (2019)
20. Edokpayi, J.N., Makungo, R., Volenzo, E.T., Rivers, T., Fhumulani, M., Odiyo, J.O.: Influence of global climate change on water resources in South Africa: towards an adaptive management approach. Chapter 5. In: P Singh, Y. Milshina, K. Tian, D. Gusain, J. Bassin (eds.). ISBN: 9780128183397. Elsevier. DOI: https://doi.org/10.1016/B978-0-12-818339-7.00005-9.
21. Ehdaie, B., Rento, C.T., Son, V., Turner, S.S., Samie, A., Dillingham, R.A., Smith, J.A.: Evaluation of a silver-embedded ceramic tablet as a primary and secondary point-of-use water purification technology in Limpopo Province. South Africa. PloS one **12**(1), 1–20 (2017)
22. Ehdaie, B., Su, Y.-H., Swami, N.S., Smith, J.A.: Protozoa and virus disinfection by silver-and copper-embedded ceramic tablets for water purification. J. Environ. Eng. **146**, 04020015 (2020)
23. Ekpunobi, U.E., Agbo, S.U., Ajiwe, V.I.E.: Evaluation of the mixtures of clay, diatomite, and sawdust for production of ceramic pot filters for water treatment interventions using locally sourced materials. J. Environ. Chem. Eng. **7**(1), 1–9 (2019)
24. Erhuanga, E., Banda, M.M., Kiakubu, D., Kashim, I.B., Ogunjobi, B., Jurji, Z., Ayoola, I., Soboyejo, W.: Potential of ceramic and biosand water filters as low-cost point-of-use water treatment options for household use in Nigeria. J. Water, Sanit.Ion Hyg. Dev. **11**, 126–140 (2021)
25. Erhuanga, E., Kashim, I.B., Akinbogun, T.L.: Development of ceramic filters for household water treatment in Nigeria. Sci. Res. **2**(1), 6–10 (2014)
26. Falah, F., Haghizadeh, A.: Hydrochemical evaluation of river water quality—a case study: Horroud River. Appl Water Sci **7**(8), 4725–4733 (2017)
27. Fewtrell, L., Majuru, B., Hunter, P.R.: A re-assessment of the safety of silver in household water treatment: Rapid systematic review of mammalian in vivo genotoxicity studies. Environ. Health **16**, 1–9 (2017)
28. GARG, M.: Water pollution in India causes and remedies. Int. J. Phys. Soc. Sci. **2**(6), 555–567 (2012)
29. Goswami, K.P., Pugazhenthi, G.: Credibility of polymeric and ceramic membrane filtration in the removal of bacteria and virus from water: A review. J. Environ. Manage. **268**, 1–18 (2020)

30. Guerrero-Latorre, L., Rusiñol, M., Hundesa, A., Garcia-Valles, M., Martinez, S., Joseph, O., Bofill-Mas, S., Girones, R.: Development of improved low-cost ceramic water filters for viral removal in the Haitian context. J. Water, Sanit.Ion Hyg. Dev. **5**(1), 28–38 (2015)
31. Halla, F.F., Massawa, S.M., Joseph, E.K., Acharya, K., Sabai, S.M., Mgana, S.M., Werner, D.: Attenuation of bacterial hazard indicators in the subsurface of an informal settlement and their application in quantitative microbial risk assessment. Environ. Int. **167**, 1–13 (2022)
32. Hill, C.L., Harris, J.D., Turner, S.S., Wason, K.L., Gaylord, A.P., Hatley, M.G., Lance, T., Hardcastle, L.T., Roberts, I.T., You, J.Y., Renneker, K.O., Edokpayi, J.N., Smith, J.A.: Field and laboratory assessment of a new electrolytic point-of-use water treatment technology. Water. **14**(7): 1-19(2022)
33. Hill, C.L., McCain, K., Nyathi, M.E., Edokpayi, J.N., Kahler, D.M., Operario, D.J., Taylor, D.D.J., Wright, N.C., Smith, J.A., Guerrant, R.L., Samie, A., Dillingham, R.A., Bessong, P.O., Rogawski Mcquade, E. T.: Impact of low-cost point-of-use water treatment technologies on enteric infections and growth among children in Limpopo, South Africa. Am. Soc. Trop. Med. Hyg. **103**, 1405–1415 (2020)
34. Issa, R. J., Schoepfer, A. P., Grisold, A., Schoepfer, A.: Collaboration between west Texas A&M University, FH Joanneum, and medical University of Graz on water quality improvement for rural areas of India. Am. Soc. Therm. Fluids Engineers: 613–622. Digital library(2020)
35. Jackson, K.N., Smith, J.A.: A new method for the deposition of metallic silver on porous ceramic water filters. J. Nanotechnol. **2018**, 1–9 (2018)
36. Jackson, K.N., Smith, J.A., Edokpayi, J.N.: New method for the deposition of metallic silver and metallic copper on full-size porous ceramic water filters. Environ. Eng. Sci. **36**, 2–11 (2019)
37. Kendarto, D.R., Mulyawan, A., Dwiratna, S., Bafdal, N., Suryadi, E.: Effectiveness of ceramic water filter pots with addition of silver nitrate to reduce of *Escherichia Coli* contents. Int. J. Adv. Sci., Eng. Inf. Technol. **9**, 526–531 (2019)
38. Kotloff, K.L., Nataro, J.P., Blackwelder, W.C., Nasrin, D., Farag, T.H., Panchalingam, S., Wu, Y., Sow, S.O., Sur, D., Breiman, R.F.: Burden and aetiology of diarrhoeal disease in infants and young children in developing countries (the Global Enteric Multicenter Study, GEMS): A prospective, case-control study. The Lancet **382**, 209–222 (2013)
39. Lange, J., Materne, T., Grüner, J.: Do low-cost ceramic water filters improve water security in rural South Africa? Drink. Water Eng. Sci. **9**, 47–55 (2016)
40. Lantagne, D.: Investigation of the Potters for Peace colloidal silver-impregnated ceramic filter: Intrinsic effectiveness and field performance in rural Nicaragua. Aleth. Environ., Allston, Massachusetts.(2021)
41. Lemons, A., Branz, A., Kimirei, M., Hawkins, T., Lantagne, D.: Assessment of the quality, effectiveness, and acceptability of ceramic water filters in Tanzania. J. Water, Sanit.Ion Hyg. Dev. **6**(2), 195–197 (2016)
42. Lyon-Marion, B.A., Mittelman, A.M., Rayner, J., Lantagne, D.S., Pennell, K.D.: Impact of chlorination on silver elution from ceramic water filters. Water Res. **142**, 471–479 (2018)
43. Maciel, P.M.F., Fava, N.D.M.N., Lamon, A.W., Fernandez-Ibañez, P., Byrne, J.A., Sabogal-Paz, L.P.: Household water purification system comprising cartridge filtration, UVC disinfection and chlorination to treat turbid raw water. J. Water Process. Eng. **43**, 1–10 (2021)
44. Madilonga, R.T., Edokpayi, J.N., Volenzo, E.T., Durowoju, O.S., Odiyo, J.O.: Water quality assessment and evaluation of human health risk in Mutangwi River, Limpopo Province, South Africa. Int. J. Environ. Res. Public Health **18**, 6765 (2021). https://doi.org/10.3390/ijerph18136765
45. Mazhar, M.A., Khan, N.A., Ahmed, S., Khan, A.H., Hussain, A., Rahisuddin, Changani, F., Yousef, M., Ahmadi, S., Vambol, V.: Chlorination disinfection by-products in municipal drinking water - A review. J. Clean. Prod. **273**: 1-13(2020)
46. Meade, R.D., Murray, A.L., Mittelman, A.M., Justine Rayner, J., Lantagne, D.S.: Accuracy, precision, cost, and acceptability of silver testing methods in ceramic filter manufacturing facilities. J. Water Health, **15**(1): 72-82(2017)
47. Meierhofer, R., Bänziger, C., Deppeler, S., Kunwar, B.M., Bhatta, M.: From water source to tap of ceramic filters—Factors that influence water quality between collection and consumption in rural households in Nepal. Int. J. Environ. Res. Public Health **15**, 1–14 (2018)

48. Mellor, J.E., Kallman, E., Oyanedel-Craver, V., Smith, J.A.: Comparison of three household water treatment technologies in San Mateo Ixtatan, Guatemala. J. Environ. Eng. **141**(5), 1–23 (2015)
49. Mittelman, A.M., Lantagne, D.S., Rayner, J., Pennell, K.D.: Silver dissolution and release from ceramic water filters. Environ. Sci. Technol. **49**, 8515–8522 (2015)
50. Mona, S., Van Halem, D., Medema, G.: Virus removal by ceramic pot filter disks: Effect of biofilm growth and surface cleaning, pp 1–7(2020)
51. Moraes, L.T.D., Paiva, E.M., Rodrigues, S.F., Rangel, J.H.G., Oliveira, M.M.: Development of nickel and silver ceramic filters supported on K10 montmorillonite clay for water disinfection. Cerâmica **66**, 474–482 (2020)
52. Moropeng, R.C., Budeli, P., Momba, M.N.B.: An integrated approach to hygiene, sanitation, and storage practices for improving microbial quality of drinking water treated at point of use: A case study in Makwane Village, South Africa. Int. J. Environ. Res. Public Health **18**(12), 1–15 (2021)
53. Moropeng, R. C., Momba, M.N.B.: Assessing the sustainability and acceptance rate of cost-effective household water treatment systems in rural communities of Makwane Village, South Africa. Crystals **10**, 1–16 (2020)
54. Mukaratirwa-Muchanyereyi, N., Tigere, W., Hokonya, N., Gusha, C., Guyo, U., Nyoni, S.: Preparation and performance characterization of ceramic/silver nanoparticle composite in water purification. Int. J. Appl. Ceram. Technol. **17**(3), 1522–1530 (2020)
55. Nair, C.S., Kani, K.M.: Evaluating the performance of locally made ceramic filters for household water treatment. Int. J. Res. Technol. Stud. **4**(6), 40–45 (2017)
56. Ndebele, N., Edokpayi, J.N., Odiyo, J.O., Smith, J.A.: Field investigation and economic benefit of a novel method of silver application to ceramic water filters for point-of-use water treatment in low-income settings. Water **13**(3), 1–18 (2021)
57. Ngasala, T.M., Masten, S.J., Cohen, C., Ravitz, D., Mwita, E.J.: Implementation of point-of-use water treatment methods in a rural Tanzanian community: A case study. J. Water, Sanit.Ion Hyg. Dev **10**(4), 1012–1018 (2020)
58. Normal, I. N.: The financial variables of water filter pot mainly raw material darmasaba clay in Btikk-Indonesia. Int. J. Econ. Financ. Issues **10**:111-124(2020)
59. Nunnelley, K., Smith, J.A., Smith, M.Y., Samie, A.: A new method for nanosilver application in ceramic water filters. World Environ. Water Resour. Congr. **2016**, 292–298 (2016)
60. Okotch, B., Elsimat, E.G.A., Gonzalez, L., Heeger, J., Dodos, J.: Are ceramic water filters effective in preventing diarrhoea and acute malnutrition among under-five children in Sudan? Waterlines **39**, 116–132 (2020)
61. Omona, S., Malinga, G.M., Opoke, R., Openy, G., Opiro, R.: Prevalence of diarrhoea and associated risk factors among children under five years old in Pader District, northern Uganda. Boston Med. Cent. Infect. Dis. **20**(37), 1–9 (2020)
62. Organization, W.H.: Safer water, better health, (2019)
63. Oskam, M.J., Pavlova, M., Hongoro, C., Groot, W.: Socio-economic inequalities in access to drinking water among inhabitants of informal settlements in South Africa. Int. J. Environ. Res. Public Health **18**, 1–19 (2021)
64. Potters Without Boarders (PWB).: Ceramic water filter program. (2019). https://www.pottersforpeace.org/ceramic-water-filter-project. Accessed 11 Oct 2022
65. PureMadi.: Dertig Facility, (2021). www.puremadi.org
66. Ramírez-Castillo, F.Y., Loera-Muro, A., Jacques, M., Garneau, P., Avelar-González, F.J., Harel, J.: Waterborne pathogens: Detection methods and challenges. Pathogens **4**(2), 307–334 (2015)
67. Ray, I., Smith, K.R.: Towards safe drinking water and clean cooking for all. Lancet Glob. Health **9**, e361–e365 (2021)
68. Ren, D., Smith, J.A.: Retention and transport of silver nanoparticles in a ceramic porous medium used for point-of-use water treatment. Environ. Sci. Technol. **47**, 3825–3832 (2013)
69. Resource Development International-Combodia (RDIC).: Ceramic water filters. (2016). https://rdic.org/water-filtration-system/. Accessed 11 Oct 2022

70. Rivera, R.: Household water treatment options in developing countries: CDC Ceramic filtration, pp 1–2(2008)
71. Rivera-Sánchez, S.P., Ocampo-Ibáñez, I.D., Silva-Leal, J.A., Flórez-Elvira, L.J., Castaño-Hincapié, A.V., Dávila-Estupiñan, A., Martínez-Rivera, J.I., Pérez-Vidal, A.: A novel filtration system based on ceramic silver-impregnated pot filter combined with adsorption processes to remove waterborne bacteria. Sci. Rep. **10**, 1–7 (2020)
72. Salsali, H., McBean, E., Brunsting, J.: Virus removal efficiency of Cambodian ceramic pot water purifiers. J. Water Health **9**, 306–311 (2011)
73. Shepard, Z.: Performance of silver nanoparticle-impregnated ceramic water filters. University of Rhode Island, (2020)
74. Simonis, J.J., Basson, A.K.: Manufacturing a low-cost ceramic water filter and filter system for the elimination of common pathogenic bacteria. Phys. Chem. Earth, Parts A/B/C **50–52**, 269–276 (2012)
75. Singh, R., Rento, C., Son, V., Turner, S., Smith, J.A.: Optimization of silver ion release from silver-ceramic porous media for household level water purification. Water **11**(4), 1–17 (2019)
76. Sobsey, M.D., Stauber, C.E., Casanova, L.M., Brown, J.M., Elliott, M.A.: Point of use household drinking water filtration: a practical, effective solution for providing sustained access to safe drinking water in the developing world. Environ. Sci. Technol. **42**, 4261–4267 (2008)
77. Soliman, M.Y.M., van Halem, D., Medema, G.: Virus removal by ceramic pot filter disks: Effect of biofilm growth and surface cleaning. Int. J. Hyg. Environ. Health **224**, 1–8 (2020)
78. United Nations International Children's Emergency Fund (UNICEF).: Household water treatment filters product guide, (2020)
79. United States Environmental Protection Agency (USEPA).: Protocol for testing microbiological water purifiers. Environmental Protection Agency, Report of Task Force, revised April, (1987)
80. van der Laan, H., van Halem, D., Smeets, P.W.M.H., Soppe, A.I.A., Kroesbergen, J., Wubbels, G., Nederstigt, J., Gensburger, I., Heijman, S.G.J.: Bacteria and virus removal effectiveness of ceramic pot filters with different silver applications in a long-term experiment. Water Res. **51**, 47–54 (2014)
81. van Halem, D., Heijman, S., Soppe, A., van Dijk, J., Amy, G.: Ceramic silver-impregnated pot filters for household drinking water treatment in developing countries: material characterization and performance study. Water Sci. Technol.: Water Supply **7**, 9–17 (2007)
82. Venis, R.A., Basu, O.D.: Mechanisms and efficacy of disinfection in ceramic water filters: A critical review. Crit. Rev. Environ. Sci. Technol. **51**(24), 2934–2936 (2021)
83. WILLIAMS, F.: Experiences with ceramic pot water filtration systems in Uganda: A case study of the health and social impacts of a market-based approach. University of Michigan, Master of Landscape Architecture (2020)
84. World Health Organization (WHO): Guidelines for drinking-water quality. World Health Organization: Geneva, Switzerland **216**, 303–304 (2011)
85. World Health Organization (WHO).: Water and sanitation for health facility improvement tool (WASH FIT): A practical guide for improving quality of care through water, sanitation, and hygiene in health care facilities. (2017)
86. World Health Organization (WHO): Safer water, better health. World Health Organization, Geneva, Switzerland (2019)
87. World Health Organization/United Nations International Children's Emergency Fund (WHO/UNICEF) Joint water supply and sanitation monitoring programme.: Progress on sanitation and drinking water: 2015 update and MDG assessment. World Health Organization, (2021)
88. Yang, H., Xu, S., Chitwood, D.E., Wang, Y.: Ceramic water filter for point-of-use water treatment in developing countries: Principles, challenges and opportunities. Front. Environ. Sci. Eng. **14**, 1–10 (2020)

89. Zaman, S., Begum, A., Rabbani, K.S., Bari, L.: Low cost and sustainable surface water purification methods using Moringa seeds and scallop powder followed by bio-sand filtration. Water Science & Technology: Water Supply **17**(1), 125–137 (2017)
90. Zinn, C., Bailey, R., Barkley, N., Walsh, M.R., Hynes, A., Coleman, T., Savic, G., Soltis, K., Primm, S., Haque, U.: How are water treatment technologies used in developing countries and which are the most effective? An implication to improve global health. J. Public Health Emerg. **2**(25), 1–14 (2018)

Natural and Modified Clay Applications in Remediation of Contaminated Groundwater and Soil Environments

Ayse Dilek Atasoy and Mehmet İrfan Yeşilnacar

Abstract Due to their tendency for adsorbing and immobilizing contaminants, clays and clay minerals can serve as materials for pollution control, factor that delay or prevent pesticide leaching into groundwater, and barriers in nuclear or hazardous waste management. Clay content of soil, along with organic matter and metal oxides control the contamination amount in surrounding and leaching solutions. Contaminants' adsorption in soil as the key process, retards their mobility and infiltration through the soil profile. Toxic metals in wastewater create environmental pollution in all over the world. Industrial discharges and mine wastes are the major sources of detrimental metals. Their adsorption on widespread and inexpensive adsorbents is the most basic and cost-effective method for water treatment. In recent years, natural or modified clays have emerged as very attractive alternatives to be used as mentioned adsorbents. Heavy metal ion uptake includes a variety of processes, like simple ion exchange, surface complexation, and surface precipitation. The infiltration of metal is conversely related to adsorption and that the mobility of contaminant in the soil is controlled by the sorption phenomenon. Heavy metal adsorption on the soil will allow its accumulation on the plants while reducing its leaching to groundwater. Application of soil amendments can be used often as one of the in-situ technologies for the remediation process of contaminated soil. Clay minerals, in many cases, can be applied as suitable sorbents for the removal of metals. Studies of reactive clay barriers have included designs for which sorption is the primary mechanism for reducing contaminant flux. Therefore, this chapter presents an overview of natural (raw) and modified clay applications for vertical reactive barriers that use adsorbing materials to remove contaminants from groundwater. Clay also appears as a good soil amendment alternative in soil remediation. It was aimed in this chapter to reveal the heavy metal removal potential of different clays and to assess the possibility of their use as an adsorbent material in water treatment. In this context, adsorption

---

Edited by Meththika Vithanage, Giuseppe Lazzara, Anushka Upamali Rajapaksha

---

A. D. Atasoy · M. İ. Yeşilnacar (✉)
Engineering Faculty, Environmental Engineering Department, Harran University, Şanliurfa, Turkey
e-mail: mirfan@harran.edu.tr

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_23

studies on the natural and modified clays were examined. The heavy metal adsorption capacities of different clay types were studied, and Freundlich and Langmuir adsorption coefficients were compared with other similar samples. Efficiency of clay as an immobilization agent for metal binding was tested by adsorption batch tests. Various pH and temperature conditions were also included in the studies. Clay as a low-cost adsorbent has been concluded as a replacement for current costly methods of removing heavy metal from water. Clay modification was done by using Na and Mg incorporated materials and calcination at different temperatures. Adsorption capacities of raw and modified clay types were compared for different contaminants, and suitability of clays for use as soil remediation amendment and as a contaminant binding surface in reactive barriers for groundwater remediation were discussed.

Keywords Clay modification · Remediation · Water treatment · Adsorbent · Adsorption isotherms

1 Introduction

Clay minerals in nature may be benefitted as cost-effective adsorbents in water treatment. Due to their high specific surface area, ion exchange capacity, and abundance in soil systems, clays play a significant role in remediation of contaminated groundwater and soil environments. Due to various problems related with the organic and inorganic anionic pollutants or the inorganic cationic pollutants, the investigations were carried out as to innovate the natural clay materials with probable modifications [32].

Clay modification is used as an effective amendment for removing different contaminants from water. Modification of soil clays to organoclays is being improved as an in-situ subsurface remediation technic. For this purpose, organic cationic solution injects to form sorptive districts that can adsorb and immobilize contaminant plumes. In various chapters, details of this technology were discussed in line with the binding of modified soil clays, the subsoil hydraulic properties, the adsorption of contaminants by modified clays, and bioavailability of adsorbed contaminants to degrading bacteria [11]. Heavy metal immobilization states to the approach of in-situ techniques that use mostly clays or applications to mitigate the heavy metal bio-utilization in soil. This process includes adsorption, precipitation, and complexation reactions, which conclude in the phase transition thereby reducing their mobility in the water and soil [10, 40].

Various clay types have been used in the storage or disposal of hazardous wastes for environment protection. Clay minerals act as a natural sweeper of contaminants with ion uptake through adsorption or anion/cation exchange [28, 53]. Various clay types such as bentonite, sepiolite, and palygorskite, are utilized as agents in the polluted agricultural soil remediation. Despite the advantages of clay minerals in remediation applications, some restrictions such as low adsorption capacity, small metal-binding constants, limited selectivity for pollutant types, and large dosages appears as a constraint. There is an immediate need to determine how the modified clays effect the remediation, how the applied dosages can be reduced to lower costs, and how this process can be improved [52].

Heavy metal contamination is an important environmental problem in all over the world. It is often used in the literature as a name set for metals and semi-metals that have been associated with potential toxicity and contamination [21]. Heavy metals can be released into the environment from a wide variety of sources. Human-based activities, mining activities, solid fuels, exhaust emissions, and industrial and domestic wastes can be listed as the main reasons for heavy metal pollution [43]. In addition, they are the main components of contaminants, such as municipal waste, sludge, fertilizers, and pesticides that polluted natural resources. They are toxic elements and can cause serious health problems to most living things [25]. Contaminated water has heavy metals, like aluminum, iron, copper, zinc, and manganese. Because of their potential toxic effects, discharged dissolved metals into the environmental resources as industrial wastewater or mine drainage water are assumed to be hazardous elements.

Adsorption has a significant impact in pollution control approaches [42]. In the recent past, wide variety of methods have been applied for economical and reliable treatment of metal-contaminated wastewater. Adsorption has emerged out to be better alternative treatment methods [49]. Moreover, it is key process on the heavy metal fate in the natural environmental resources. Soil adsorbed contaminants are somewhat immobile in the soil and they have low infiltration rate through the soil horizons. The heavy metal infiltration is conversely related to its adsorption potential and that the contaminant mobility in the soil is controlled by the sorption phenomenon. Adsorption is principally a mass transfer case by which an element is transferred from the aqueous phase to the solid surface, and becomes bound by physical or chemical bonds [8]. Heavy metal removal by adsorption techniques has significant advantages, such as availability, profitability, high efficiency, ease of operation, and low cost in comparison with other technique [12]. This chapter aims to present an overview of natural (raw) and modified clay applications for contaminant removal from soil and groundwater by vertical reactive barriers including adsorbing materials, and to examine the adsorption studies on the natural and modified clays to reveal the heavy metal removal potential of different clays and to assess the possibility of their use as an adsorbent material in water treatment.

Kasgoz et al. [29] and Mockovciakova et al. [36] claimed the clay and clay composites as high-impact adsorbents for heavy metal removal from water. Clays also have high cation exchange capacity (CEC) providing the efficient adsorptive character [47]. Negatively charged clay minerals are widely used in the removal of metal cations from wastewater in view of their high surface area and exchangeable cations [53].

2 Natural and Modified Clays

Natural and modified forms of clays have been extensively used for wastewater treatment technologies. Natural materials like activated carbons, clay minerals, and agricultural and industrial wastes have been employed as adsorbents in wastewater treatment [41]. The clay minerals have got a lot of attention as efficient adsorbents for contaminants in wastewaters [7]. Although natural clays have been widely used for water treatment, its hydrophilic surface usually renders in poor removal efficiency [50, 56]. Therefore, modified raw clays which have enhanced adsorption affinity toward different contaminants were investigated in various studies. The natural clay structure and surface properties were modified via chemical or thermal process.

Atasoy and Sahin [3] investigated the fluoride (F) adsorption by the raw and the modified local cement clay. They used raw clay (CR) in their study that was currently utilized in cement production as local materials procured from Yaylak, Sanliurfa, Turkiye. Modified clays were arranged through calcination (500 and 850 °C), incorporation with Na and Mg, and application of both processes. Low F adsorption (with K_f_Freundlich constant and Q_0_Langmuir constant values of 0.10 and 0.80, respectively) was achieved on the CR due to the clay's negative charged sites, which make it poor adsorbent for anions like F. Na or Mg incorporation into CRs or calcination alone did not show a significant change in the F adsorption rates. However, Mg saturation of CR and then calcination at 500 °C increased the F adsorption, significantly with Q_0 and K_f values of 1.69 and 0.27, respectively. Calcination created the stringent bonds between the cations and the clay particulates. This issue resulted in the increased adsorption of F on the positive sites.

In a similar investigation, Atasoy et al. [4] researched the fluoride adsorption by batch method on the raw bauxite (BR) and the modified bauxite. Bauxite modification was formed by incorporation with Na (B-Na) and Mg (B-Mg) and calcination of Mg incorporated bauxite at 500 °C (B-Mg-500). They found the highest F adsorption capacity for Mg incorporated bauxite at 500 °C (Fig. 1). This phenomenon was explained by the increased vacant sites and adsorbed Mg ions in the incorporated bauxite with the calcination treatment.

Froehner et al. [22] investigated the phenol removal potential of modified vermiculite and bentonite from contaminated water. Modified clays were synthesized by insertion of hexadecyltrimethylammonium in clay layers. The natural inorganic cations were replaced with organic cations to improve the adsorbent properties. The hydrophobic modified vermiculite was found very effective for phenol removing from water. The non-modified clays showed insignificant interaction with phenol. The removal percentage of modified vermiculite was higher than 35%, while it was 30% for modified bentonite.

The natural clay can be modified with distinct organic molecules by exchanging reactions of exchangeable cations or incorporated with organic molecule as to functionalize the surface of clay. The incorporation of these organic molecules may finally rise the interlayer space of clay and hence allow the higher specific surface area and the affinity toward several contaminants present in aqueous solution [57].

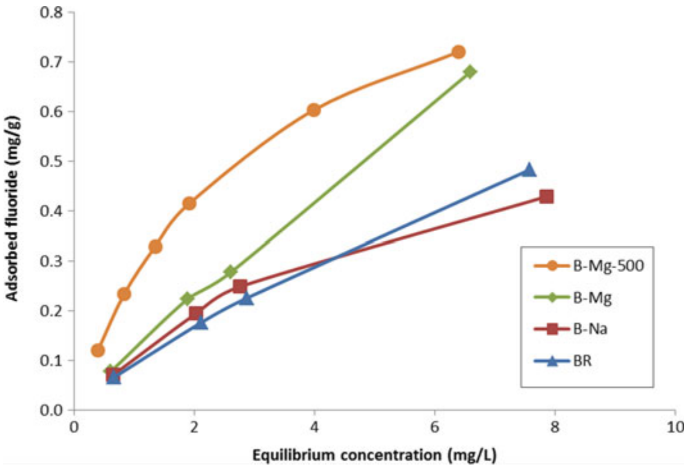


Fig. 1 Fluoride adsorption capacity of raw and modified bauxite [4]

3 Clays in Remediation Technologies

Clay content of soil renders the soil-applied contaminants less bioavailable due to increased adsorption. Adsorption in soil reduces the leaching of contaminant through the deep horizons toward the groundwater [45]. Adsorption is a quick and changeable mechanism for the removal of harmful anions or cations from groundwater by effective adsorptive clay barriers. Adsorption provides a solution to groundwater as well as soil remediation [19]. Using clay amendments to remediate soil will increase the adsorption of pesticides and heavy metals reducing their bio-availability and efficacy, but also reducing their tendency to leach into root zones of deep-rooted crops and into groundwater [24].

Immobilization systems are intended to reduce contaminant mobility by modifying the physical or leaching properties of the soil system [15]. Movement is typically reduced by either physically limiting interaction between the pollutant and the ambient groundwater or chemically changing the pollutant to render it more suitable for groundwater dissolution. Metals' solid-phase as well as aqueous chemistry lends itself to immobilization through these strategies. Metal pollutants can be immobilized using a number of approaches, comprising those that utilize natural, thermally, or chemically modified clay reagents to directly attach the polluted soil or slurry [51]. The majority of immobilization approaches could be done either in situ or ex situ. In situ methods are favored because they require less manpower and resources, but their applications would be dependent on complex site situations [1]. Mudzielwana et al. [37] prepared surfactant-modified kaolin clay for As(III) and As(V) by intercalating hexadecyltrimethylamonium bromide (HDTMA-Br) cationic surfactant onto the clay interlayers. It has been proven that surfactant-modified kaolin clay was a candidate adsorbent for arsenic remediation from groundwater.

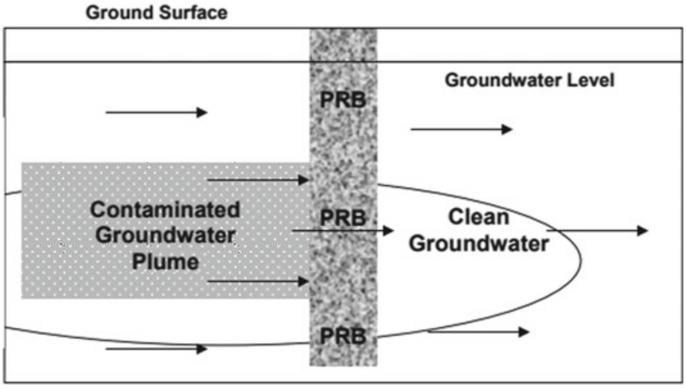


Fig. 2 Permeable reactive barrier configuration [13]

Raw and modified clays are efficient materials for reactive barriers' media in remediation applications. A permeable Reactive Barrier (PRB) is a reactive wall or zone constructed below ground to remediate contaminated groundwater (Fig. 2). This trench is filled with reactive media that adsorbs pollutants migrating with the natural flow of the groundwater. Once backfilled with the selected media, the trench is then covered with soils, plants, and the area is returned to its natural condition. Contaminants are contained within this treatment zone, reducing the threat of downgradient contamination [13].

Atasoy and Bilgic [2] studied on bauxite and montmorillonite clay. They found a greater adsorption capacity for the bauxite than the montmorillonite for Cu and Zn. Studied raw materials were the low-cost adsorbents that used effectively for Cu and Zn removal. Both the montmorillonite and bauxite were suggested as alternative adsorptive barrier media for Cu, Zn, or other metals contaminated sites. Clays can be used as remedial agents to grade up the old mining areas preventing the vertical transportation of metals through the groundwater, or to isolate the leachate of urban waste. pH is an important factor in soil for metal precipitation and metal adsorption cases. Cu and Zn adsorption on the clays was high at 8 pH and above. Therefore, e.g., lime application in contaminated fields to adjust the pH was affirmed to be effective for pollution management processes. In another similar study, Park and Shin [39] modified diatomite and montmorillonite by iron and manganese oxide to be used as immobilization ingredient for remediate the contaminated soil with Pb. Batch method was applied to examine the surface modification effect on Pb adsorption. Higher Pb adsorption in modified clays was determined than that in natural clays.

4 Heavy Metal Removal by Adsorption on Different Clays

4.1 Adsorption on Montmorillonite

Natural minerals, including clay minerals and zeolites, from different areas of the world have been studied for the heavy metal removal by adsorption and ion exchange processes [9]. Clay minerals such as illite, kaolinite, or montmorillonite from Algeria, Brazil, China, Pakistan, Serbia, Thailand, and Tunisia were proven efficient in removing Cd^{2+}, Cr^{3+}, Cr^{6+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, or Zn^{2+} from contaminated waters [8, 16, 17, 26, 27, 34, 46]. Montmorillonite has excellent adsorptive properties because of its structural characteristics. It has especially a large surface area, more tight channels inside, and wide adsorption sites within its inner space [44]. Mermut et al. [35] stated that Southeastern Turkey soils typically contained 60–65% clay, and montmorillonite was the most common clay type. Atasoy and Bilgic [2] investigated Cu and Zn adsorption on montmorillonite, and the usability of this adsorbent in heavy metal removal from water was discussed. It has the potential to be effectively used to generate inexpensive materials for copper and zinc removal. They provided montmorillonite purified from all of the impurities from Soil Science Department in University of Saskachewan, Canada. It matches to the 2:1 clay family and is formed of two tetrahedral coordinated sheets of silicon ions surrounding a sandwiched octahedral coordinated aluminum ions sheet. Net surface charge in the clay was negative because of the isomorphouse substitution occurred in the tetrahedral layers by substitution of Al^{+3} for Si^{+4} and in the octahedral layer by substitution of divalent cation such as Mg^{+2} for Al^{+3}. High Cu and Zn adsorption rates were found on montmorillonite. Maximum Cu and Zn adsorption were 98.67 and 98.55%, respectively. Montmorillonite adsorption capacity for Cu was higher than Zn with Q_o and K_f values of 8.136 and 1.978 mg g^{-1}, respectively (Table 1).

Çelik [14] studied Pb and Ni removal potential of montmorillonite from water below the certain concentration. The equilibration time for both of the metal adsorption on montmorillonite took 20 min. Once the equilibrium was reached, maximum Pb and Ni adsorption rates were 97.74 and 75.30% on montmorillonite, respectively (Fig. 1). Increase in Pb and Ni adsorption was noted with increasing doses of adsorbents. Lead and Ni adsorption fitted well with both of Freundlich and Langmuir

Table 1 Cu–Zn adsorption and Freundlich and Langmuir constants [2]

Clays	Isotherm models					
	Langmuir parameters			Freundlich parameters		
	Q_0 (mg g^{-1})	b (L mg^{-1})	R^2	K_f (mg g^{-1})	N	R^2
Bauxite (Cu)	9.115	0.757	0.98	4.179	4.098	0.97
Montmorillonite (Cu)	8.136	0.402	0.96	1.978	2.088	0.96
Bauxite (Zn)	5.197	1.095	0.99	2.882	6.230	0.96
Montmorillonite (Zn)	4.290	0.386	0.95	1.868	2.037	0.98

Table 2 Langmuir and Freundlich constants of Pb and Ni adsorption on Montmorillonite and clay brick [14]

Clays	Isotherm models					
	Langmuir parameters			Freundlich parameters		
	Q_0 (mg g^{-1})	b (L mg^{-1})	R^2	K_f (mg g^{-1})	n	R^2
Montmorillonit (Pb)	37.313	0.252	0.98	7.967	2.911	0.86
Clay Brick (Pb)	25.062	7.634	0.98	9.729	5.637	0.90
Montmorillonit (Ni)	24.938	0.028	0.97	1.548	2.045	0.97
Clay Brick (Ni)	3.398	0.169	0.97	1.029	3.341	0.98

isotherms. Lead adsorption was found to be higher than Ni. The montmorillonite maximum adsorption capacity for Pb and Ni was 37.31 mg g^{-1} and 24.94 mg g^{-1}, respectively (Table 2).

4.2 Adsorption on Bauxite Clay

Bauxite is claylike material, and it has varieties in colors ranging from white to brown or red. Furthermore, it was used as an adsorbent for the removal of different trace elements, arsenic and chromate [23, 33, 54]. It is abundantly available mineral mostly containing alumina, iron, silica and titanium oxides. Al in its content ranges between 50 % and 70 % [20]. Atasoy and Bilgic [2] researched Cu and Zn adsorption on bauxite and removal from water. Atasoy et al. [4] studied with raw and modified bauxite in their research for drinking water. The bauxite used in both studies was a regional material purchased from Aluminum Process Plant in Eskisehir, Turkey. Bauxite is easy accessible in Turkey. Air-dried and sieved (<2 mm) bauxite was prepared in Istanbul Technical University, Geological Engineering Laboratories. According to its X-ray diffractogram, it comprised of boehmite, kaolinite, calcite, and hematite as 32.4%, 26%, 24.1%, and 21.1%, respectively. High adsorption rates for metals on bauxite were achieved by Atasoy and Bilgic [2]. Maximum adsorption of Cu and Zn was 99.65 and 99.41%, respectively (Fig. 1). They found the maximum adsorption for Cu on bauxite (Kf: 4.179 mg g^{-1}; the maximum adsorbed capacity (Qo) estimated by Langmuir model achieved 9.115 mg g^{-1} (Table 1). Klauber et al. [30] claim that alkalinity supports metals precipitation as hydroxides and carbonates, while the large amount of iron/aluminum oxides supplies surface sites for metals' sorption reactions. High iron and aluminum concentrations in bauxite and its alkalinity conduce to its high adsorption potential. Atasoy et al. [4] prepared modified bauxite by using Mg and Na incorporation of bauxite (B–Mg, B–Na) and 500 °C calcined Mg incorporated bauxite (B–Mg-500). Adsorption increased with the rising adsorbent dose, and adsorption isotherms matched well with the Freundlich model. Raw and incorporated bauxites' adsorption capacities were found low for metals.

Thakre et al. [48] explained this phenomenon with easy desorption from the positive sites or mainly the weaker physical bonds between adsorbates and adsorbents [3]. In contrast, the maximum adsorption was achieved for calcined incorporated bauxite (with Mg) at 500 °C with Kf value of 0.247. The calcination treatment probably increased the vacant sites of incorporated bauxite to be adsorbed Mg ions. This investigation was clarified by the high number of positively charged sites in B–Mg-500.

4.3 Adsorption on Clay Brick

Renovation and demolition of old infrastructures cause high amounts of construction and demolition waste to be dumped in the environment, creating numerous environmental and social issues [31]. Excessive clay bricks have been produced in recent years in the world, most of which will be demolished in the next years [18]. Therefore, scientist and researchers are giving more attention to the effective use of waste clay bricks [31]. Additionally, studies with clay brick focused mainly to set an added value for the waste clay bricks as low-cost adsorbents to refine contaminated water.

Çelik [14] investigated the heavy metal removal potential of inexpensive adsorbent of local clay brick as replacements for current costly methods of removing the excess Pb and Ni from water below the certain concentration. It was preferred because of its low cost, abundance, and easy availability characteristic. In the study conducted with batch adsorption experiments, the effects of factors such as adsorption time, adsorbent dosage, initial metal concentration and pH were investigated. Equilibration time for Pb adsorption took 40 minutes and Ni adsorption on clay brick took 4 h. Once the equilibrium was reached, maximum Pb and Ni adsorption rates were 98.65% and 45.89%, respectively (Fig. 3). Increase in Pb and Ni adsorption was noted with increasing doses of adsorbents. There was no significant change in Pb adsorption rate, while Ni adsorption increased with the increasing pH. Lead and Ni adsorption fitted well with isotherms of both Langmuir and Freundlich. The maximum clay brick adsorption capacity was 25.06 and 3.40 mg g^{-1} for Pb and Ni, respectively (Table 2). Clay brick adsorbed higher Pb concentration than Ni.

Similar adsorption research with brick clay was carried out by Priyantha and Bandaranayaka [38]. 200 °C fired brick clay obeyed both isotherms with high regression coefficients. Negatively charged fired brick clay indicated affinity against Cr species despite the negative charged Cr ion. It was concluded that fired brick clay at 200 °C exhibited high Cr adsorption capacity. They suggested that their study may be improved for Cr (VI) contaminated effluents treatment.

Final disposal of clays that adsorb heavy metals in a way that does not cause environmental pollution is also an important problem. In this context, it is a very environmental solution to use the adsorbent in brick making as a final disposal method. Adsorbed heavy metals are confined between layers with heat treatment in the brick production. Thanks to the bricks used as building material, the release of trapped heavy metals to the environment can be prevented.

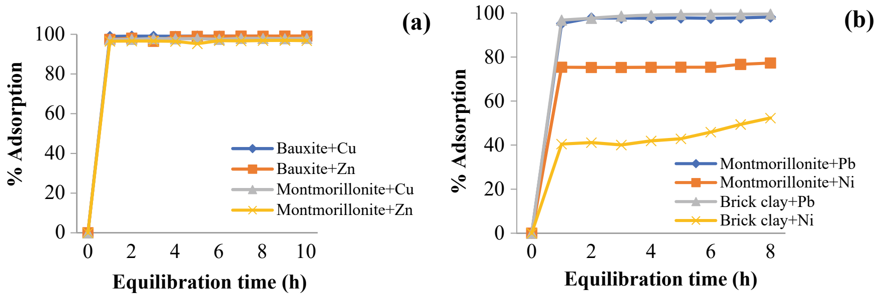


Fig. 3 Time-dependent adsorption values of **a** Cu, Zn on Bauxite and Montmorillonite and **b** Pb, Ni on cay brick and Montmorillonite [5]

4.4 Adsorption on Clayey Vertisol Soil

The soils' metal adsorption ability from liquids is of exclusive attention and has results for environmental questions like remediation of polluted soils and waste deposition. Major zones included in soils for heavy metal adsorption are mainly clays as inorganic colloids and organic colloidal material and metal oxides [12].

Atasoy et al. [6] studied on the carbonate-rich clayey soils for Fe, Mn, and Cd adsorption. Soil samples were taken from different three regions in Sanliurfa, southeast of Turkey. Vertisols as the predominant soils in the region were heavy-textured and dark-colored as found ones in arid and semi-arid regions. They contain smectite type clay and low level of organic content. The maximum adsorption of metals of Fe, Mn and Cd was found with Kf values of 16.63, 2.18, and 1.01, respectively (Table 3). The soil carbonate content showed a higher affinity than clay for Fe and Mn, while on the Cd adsorption, the clay was found to be more accelerate efficacious than the carbonate. Adsorption of Mn fitted well with isotherms of both Langmuir and Freundlich models (R2$\geq$0.95). Cd adsorption gave a better fit to the Langmuir model (R2$\geq$0.99), while Fe adsorption was better matched to the Freundlich model (R2$\geq$0.92).

The tasks of the barrier are waste storage and reducing or weakening the hazardous leachate effect to reach the groundwater during or after the existence of the landfill. Geological barriers for heavy metals and municipal solid waste landfills play an important role for the waste disposal protection and safety issues. Therefore, soils rich in clay minerals are probable geological barriers in landfills [55].

5 Conclusions

Various clay materials have been generally investigated to minimize the expensive adsorbents usage. Adsorption is one of the most important processes of metal uptake at the mineral-solute interface. Batch adsorption experiments in the recent

Table 3 Freundlich and Langmuir isotherm constants for metal adsorption on clayey vertisol soils [6]

Soil	Freundlich constants			Langmuir constants		
	K_f (mg g^{-1})	n	R^2	Q_0 (mg g^{-1})	B (L mg^{-1})	R^2
Cd						
Soil 1	0.67	1.67	0.8	2.75	2.39	0.99
Soil 2	0.74	2.38	0.8	2.46	1.99	0.99
Soil 3	1.01	2.38	0.7	2.83	17.16	0.99
Fe						
Soil 1	16.63	0.43	0.95	0.45	9.58	0.85
Soil 2	4.09	0.55	0.92	0.62	9.34	0.69
Soil 3	9.20	0.42	0.95	0.41	7.34	0.65
Mn						
Soil 1	1.56	2.16	0.99	3.13	0.20	0.95
Soil 2	2.18	2.16	0.98	2.59	0.15	0.97
Soil 3	1.35	2.14	0.99	3.21	0.29	0.95

works reported the maximum adsorption capacities for heavy metals. In the reported studies, the pH, contact time, initial concentration, temperature, and dosage effects were examined to verify the capacity of clay materials and the adsorption process with Langmuir and Freundlich isotherms. Inexpensive clay adsorbents in their high removal potentials will gain an important place as replacements for current costly methods in environmental engineering. Therefore, because of their abundance, low cost, and easy availability characteristics, clays will find intensive use against other methods in water treatment. Raw and modified clay minerals have important advantages in the polluted soil/groundwater remediation. They can serve as materials for pollution control due to their tendency for adsorbing and immobilizing the contaminants. Pesticide and heavy metal leaching into groundwater can be prevented by clay in the permeable reactive barrier's media. They are used in nuclear or hazardous waste management. The adsorbent properties of clays can be improved by different amendments, and higher pollutant adsorption is determined in modified clays than that in natural clays. However, remaining problems such as assessment of remediation effects using new methods, long-term reliability, and improvement of clay minerals should be the focal point of future research.

References

1. Abubaker, S.R., Atasoy, A.D.: Contaminant removal processes from soil. Soil Stud. **11**(1), 35–42 (2022)
2. Atasoy, A.D., Bilgic, B.: Adsorption of copper and zinc ions from aqueous solutions using montmorillonite and bauxite as low-cost adsorbents. Mine Water Environ. **37**, 205–210 (2018)
3. Atasoy, A.D., Sahin, M.O.: Adsorption of fluoride on the raw and modified cement clay. Clean–Soil, Air, Water **42**(4), 415–420 (2014)
4. Atasoy, A.D., Yesilnacar, M.I., Sahin, M.O.: Removal of fluoride from contaminated ground water using raw and modified bauxite. Bull Environ. Contam. Toxicol. **91**, 595–599 (2013)
5. Atasoy, A.D., Karabulut, B.Y.: Adsorption of heavy metals with various porous materials. Süleyman Demirel Univ., J. Nat. Appl. Sci. **23**(2), 427–432 (2019)
6. Atasoy, A.D., Sagir, M., Erdem, A.F.: Adsorption of Fe, Mn and Cd in carbonate-rich clayey soils and assessment of environmental effects. Environ. Eng. Manag. J. **18**(12), 2605–2611 (2019)
7. Awad, A.M., Shaikh, S.M.R., Jalab, R., Gulied, M.H., Nasser, M.S., Benamor, A., Adham, S.: Adsorption of organic pollutants by natural and modified clays: a comprehensive review. Sep. Purif. Technol. **228**, 115719 (2019)
8. Babel, S., Kurniawan, T.A.: Various treatment technologies to remove arsenic and mercury from contaminated groundwater: an overview. In: Proceedings of the First International Symposium on Southeast Asian Water Environment, 24–25 October, Bangkok, Thailand, pp. 433–440 (2003)
9. Bedelean, H., Maicaneanu, A., Burca, S., Stanca, M.: Removal of heavy metal ions from wastewaters using natural clays. Clay Miner. **44**, 487–495 (2009)
10. Bolan, N., Kunhikrishnan, A., Thangarajan, R., Kumpiene, J., Park, J., Makino, T., Kirkham, M.B., Scheckel, K.: Remediation of heavy metal(loid)s contaminated soils—to mobilize or to immobilize? J Hazard Mater. **266**, 141–166 (2014)
11. Boyd, S.A.: In-situ clay modification for environmental remediation. In: Conference: Spring national meeting of the American Chemical Society (ACS), 24–28 March, New Orleans, LA (United States) (1996)
12. Bradl, H.B.: Adsorption of heavy metal ions on soils and soils constituents. J. Colloid Interf. Sci. **277**, 1–18 (2004)
13. Bullock, A.M.: Innovative uses of organophilic clays for remediation of soils, sediments and groundwater. In: WM' 07 Conference, February 25–March 1, Tucson AZ (2007)
14. Çelik, A.Z.: Adsorption of lead and nickel on the natural clays. Harran University, Institude of Science, Environmental Engineering, Şanlıurfa, Turkiye (2014)
15. Cabrejo, E., Phillips, E.: In Situ remediation and stabilization technologies for mercury in clay soils, Student Summer Internship Technical Report, DOE-FIU Science & Technology Workforce Development Program, US Department of Energy (2010)
16. Chaari, I., Fakhfakh, E., Chakroun, S., Bouzid, J., Boujelben, N., Feki, M., Rocha, F., Jamoussi, F.: Lead removal from aqueous solutions by a tunisian smectitic clay. J. Hazard. Mater. **156**, 545–551 (2008)
17. Chantawong, V., Harvey, N.W., Bashkin, V.N.: Comparison of heavy metal adsorptions by Thai kaolin and ballclay. Water Air Soil Pollut. **148**, 111–125 (2003)
18. Chen, M.Z., Lin, J.T., Wu, S.P., Liu, C.H.: Utilization of recycled brick powder as alternative filler in asphalt mixture. Constr. Buil. Mater. **25**, 1532–1536 (2011)
19. Dardouri, S., Sghaier, J.: Adsorption characteristics of layered soil as delay barrier of some organic contaminants: experimental and numerical modeling. Environ. Model. Softw. **110**, 95–106 (2018)
20. Dixon, J.B., Schulze, D.G.: Soil Mineralogy with Environmental Applications. SSSA, Inc., Madison, p. 866 (2002)
21. Duffus, J.H.: Chem. Int. **23**(6), 161–167 (2001)
22. Froehner, S., Martins, R.F., Furukawa, W., Errera, M.R.: Water remediation by adsorption of phenol onto hydrophobic modified clay. Water Air Soil Pollut. **199**, 107–113 (2009)

23. Giles, D.E., Mohapatra, M., Issa, T.B., Anand, S., Singh, P.: Iron and aluminium based adsorption strategies for removing arsenic from water. J. Environ. Manag. **92**(12), 3011–3022 (2011)
24. Goldberg, S. In: E.A. Jenne (ed.), Adsorption of Heavy Metals by Geomedia, Academic Press, San Diego (1998)
25. Gu, S., Kang, X., Wang, L., Lichtfouse, E., Wang, C.: Clay mineral adsorbents for heavy metal removal from wastewater: a review. Environ. Chem. Lett. **17**, 629–654 (2019)
26. Hongping, H., Jiugao, G., Xiande, X., Jinlian, P.: Experimental study of the selective adsorption of heavy metals onto clay minerals. Chin. J. Geochem. **19**, 105–109 (2000)
27. Ikram, M., Rauf, M.A., Rauf, N.: Trace level removal studies of Cr (III) from aqueous solution. J. Trace Microprobe Tech. **20**, 119–125 (2002)
28. Ismadji, S., Soetaredjo, F.E., Ayucitra, A.: Clay Materials for Environmental Remediation. Springer International Publishing, Cham (2015)
29. Kasgoz, H., Durmus, A., Kasgoz, A.: Enhanced swelling and adsorption properties of AAm-AMPSNa/clay hydrogel nanocomposites for heavy metal ion removal. Polym. Adv. Technol. **19**(3), 213–220 (2008)
30. Klauber, C., Grafe, M., Power, G.: Review of bauxite residue "Reuse" options. CSIRO document DMR-3609, project ATF-06-03, management of bauxite residues. Department of Resources, Energy and Tourism (DRET), Australia (2009)
31. Kumara, G.M.P., Kawamoto, K.: Applicability of crushed clay brick and municipal solid waste slag as low-cost adsorbents to refine High concentrate cd (ii) and pb (ii) contaminated wastewater. Int. J. Geomate **17**(63), 133–142 (2019)
32. Lee, S.M., Tiwari, D.: Organo and inorgano-organo-modified clays in the remediation of aqueous solutions: an overview. Appl. Clay Sci. **59**(60), 84–102 (2012)
33. Mayes, W.M., Jarvis, A.P., Burke, I.T., Walton, M., Feigl, V., Klebercz, O., Gruiz, K.: Dispersal and attenuation of trace contaminants downstream of the Ajka bauxite residue (red mud) depository failure Hungary. Environ. Sci. Technol. **45**(12), 5147–5155 (2011)
34. Mello Ferreira Guimaraes, A., Ciminelli, V.S.T., Vasconcelos, W.L.: Smectite organofunctionalized with thiol groups for adsorption of heavy metal ions. Appl. Clay Sci. **42**, 410–414 (2009)
35. Mermut, A.R., Padmanabham, E., Eswaran, H., Dasog, G.S.: Pedogenesis. In: Ahmad, N., Mermut, A. (eds.) Vertisols and Technologies for Their Management Development in Soil Science, pp. 43–61. Elsevier, Amsterdam (1996)
36. Mockovciakova, A., Orolinova, Z., Skvarla, J.: Enhancement of the bentonite sorption properties. J. Hazard. Mater. **180**(1–3), 274–281 (2010)
37. Mudzielwana, R., Gitari, M.W., Ndungu, P.: Performance evaluation of surfactant modified kaolin clay in As(III) and As(V) adsorption from groundwater: adsorption kinetics, isotherms and thermodynamics. Heliyon **5**, e02756 (2019)
38. Priyantha, N., Bandaranayaka, A.: Interaction of Cr (VI) species with thermally treated brick clay. Environ. Sci. Pollut. Res. **18**, 75–81 (2011)
39. Park, J.H., Shin, W.S.: Immobilization of Pb contaminated soil using modified clay. Water Pract. Technol. 1, 2 wpt2006035 (2006). https://doi.org/10.2166/wpt.2006.035
40. Rahman, I.M.M., Begum, Z.A., Sawai, H..: Chapter 6: solidification/stabilization: a remedial option for metal contaminated soils. In: Hasegawa, H., Rahman, I.M.M., Rahman, M.A. (eds.) Environmental Remediation Technologies for Metal-Contaminated Soils. Springer Japan, Tokyo. pp. 125–146 (2016)
41. Rashed, M.N.: Adsorption technique for the removal of organic pollutants from water and wastewater, In: Rashed, M.N. (ed.) Organic pollutants—Monitoring, risk and treatment, pp. 167–179. Intech Open, Croatia (2013)
42. Reddad, Z., Gerente, C., Andres, Y., Le, C.P.: Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. Environ. Sci. Technol. **36**(9), 2067–2073 (2002)
43. Şahinkaya, E., Bayrakdar, A., Güngör, M., Yücesoy, Z., Uyanık, S., Yeşilnacar M.I., Atasoy, A.D.: Formation of acidic mine leachate (ams), active treatment systems and metal recovery. In: 3rd Mining and Environment Symposium, Ankara, pp. 108–116 (2009)

44. Seliman, A.F., Lasheen, Y.F., Youssief, M.A.E., Abo-Aly, M.M., Shehata, F.A.: Removal of some radionuclides from contaminated solution using natural clay: bentonite. J. Radioanal. Nucl. Chem. **300**, 969–979 (2014)
45. Shi, Z., Zhang, F., Wang, C.: Adsorption of phenanthrene by earthworms—A pathway for understanding the fate of hydrophobic organic contaminants in soil-earthworm systems. J. Environ. Manag. **212**, 115–120 (2018)
46. Sljivic, M., Smiciklas, I., Pejanovic, S., Plecas, I.: Comparative study of Cu2+ adsorption on a zeolite, a clay and a diatomite from Serbia. Appl. Clay Sci. **43**, 33–40 (2009)
47. Srinivasan, R.: Advances in application of natural clay and its composites in removal of biological, organic, and inorganic contaminants from drinking water. Adv. Mater. Sci. Eng. **19**(3), 213–220 (2011)
48. Thakre, D., Rayalu, S., Kawade, R., Meshram, S., Subrt, J., Labhsetwar, N.: Magnesium incorporated bentonite clay for defluoridation of drinking water. J. Hazard. Mater. **180**, 122–130 (2010)
49. Tripathi, A., Ranjan, M.R.: Heavy metal removal from wastewater using low cost adsorbents. J. Bioremed. Biodeg. **6**(6), 1–5 (2015)
50. Yang, Q., Gao, M., Zang, W.: Comparative study of 2,4,6-trichlorophenol adsorption by montmorillonites functionalized with surfactants differing in the number of head group and alkyl chain. Colloids Surf. A Physicochem. Eng. Asp. **520**, 805–816 (2017)
51. Yang, X., Liu, L., Tan, W., Liu, C., Dang, Z., Qiu, G.: Remediation of heavy metal contaminated soils by organic acid extraction and electrochemical adsorption. Environ. Pollut. **264**, 114745 (2020)
52. Yi, X., Xuefeng, L., Yingming, X., Xu, Q., Qingqing, H., Lin, W., Yuebing, S.: Remediation of heavy metal-polluted agricultural soils using clay minerals: a review. Pedosphere **27**(2), 193–204 (2017)
53. Yuan, G.D., Theng, B.K.G., Churchman, G.J., Gates, W.P.: Chapter 5.1—Clays and clay minerals for pollution control. In: Bergaya, F., Theng, B.K.G., Lagaly, G. (eds.) Handbook of Clay Science, pp. 587–644. Elsevier, Amsterdam (2013)
54. Yuhua, W., Ye, L., Yuehua, H.: Adsorption mechanisms of Cr (VI) on the modified bauxite tailings. Miner. Eng. **21**, 12–14, special issue: SI, 913–917 (2008)
55. Zaki, A.A., Ahmad, M.I., Abd El-Rahman, K.M.: Sorption characteristics of a landfill clay soil as a retardation barrier of some heavy metals. Appl. Clay Sci. **135**, 150-167 (2017)
56. Zhang, L., Zhang, B., Wu, T., Sun, D., Li, Y.: Adsorption behavior and mechanism of chlorophenols onto organoclays in aqueous solution. Colloids Surf. A Physicochem. Eng. Asp. **484**, 118–129 (2015)
57. Zohra, B., Aicha, K., Fatima, S., Nourredine, B., Zoubir, D.: Adsorption of direct Red 2 on bentonite modified by cetyltrimethylammonium bromide. Chem. Eng. J. **136**, 295–305 (2008)

Slow Release-Formulations for Weed and Pest Control by Clay Composites

Randima Edussuriya, S. Keerthanan, Anushka Upamali Rajapaksha, and Meththika Vithanage

Abstract Pesticides and weedicides are important agrochemicals for achieving global food supply. However, the rapid release of the active ingredient from commercial formulations, and the huge losses due to volatilization, photodegradation, and leaching, may render agrochemical usage economically unsustainable. Moreover, heavy usage of agricultural chemicals has led to serious ecological pollution. The findings of pesticide controlled/slow-release formulations are a significant concern in the modern agroindustry. Clay minerals are natural and relatively cheap components of soils. They are ideal materials for photostabilized agrochemicals and controlled release (CR) because of their colloidal nature, strong adsorption power, and easily modifiable surfaces. Clay-based formulations of pesticides can reduce their leaching, photodegradation, and volatilization. Consequently, they can improve the efficiency of agricultural chemicals and reduce environmental pollution. This book chapter discusses the potential use of nanoclay and clay composites in controlled-release pesticide/weedicide formulations, their slow-release mechanisms, challenges, and future perspectives.

Keywords Controlled-release formulations · Nanopesticides · Clay minerals · Active ingredients

---

R. Edussuriya · S. Keerthanan · A. U. Rajapaksha · M. Vithanage (✉)
Ecosphere Resilience Research Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, Nugegoda 10250, Sri Lanka
e-mail: meththika@sjp.ac.lk

A. U. Rajapaksha
Instrument Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, Nugegoda 10250, Sri Lanka

M. Vithanage
Sustainability Cluster, School of Engineering, University of Petroleum & Energy Studies, Dehradun, Uttarakhand 248007, India

Institute of Agriculture, University of Western Australia, Perth WA6009, Australia

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_24

1 Weed and Pest Control in Agricultural Systems

Crop production is a crucial part of agriculture, which ensures the global food supply. There is an increasing need for sophisticated agricultural practices that are sustainable economically and environmentally due to the scarcity of resources (such as agricultural land, soil, and irrigation system) and insufficient crop productivity [1]. Weeds are one of the main factors restricting food production in farming systems all over the world. By competing with plants for water, nutrients, and sunlight, weeds impede the growth of crops, causing significant losses in crop production [2]. Weed control is a significant challenge in agriculture, and it is often a complex, contentious and costly problem to solve. Organisms known as pests are those that compete with crops and affect harmful ways to crop growth and yield. Pests include rodents from vertebrates as well as some types of nematodes, snails, vines, and mites, and the most prevalent category is insects. They result in less crop density, stunted growth, a lesser capacity for production, and a reduction in the yield or quality of horticultural goods [3]. Crop losses are significantly higher in tropical nations because of the high temperatures and humidity, there are ideal conditions for pests to multiply rapidly [4]. Since both weeds and pests can have a negative impact on horticultural operations. Weed and pest management have been recognized as important aspect in sustainable agriculture.

1.1 Methods of Weed and Pest Control

Currently, two main strategies correspond to different techniques in weed management in agricultural systems. On the one hand, synthetic weedicides are commonly used, but on the other, mechanical, cultural, and physical methods are frequently used to manage weeds [5]. Mechanical weed control techniques are challenging and need various weeding techniques and crop production strategies to achieve economically acceptable weed control levels. Mechanical weed control destroys weeds or reduces their competitive ability via physical means [6]. The crop, soil type, running costs, and demand of the workforce are a few practical factors that influence the choice of the mechanical weeding technique [7]. The use of herbicides or weedicides, also known as chemical substance applications, is at the top of weed control methods. Weedicides were introduced in agriculture mainly to combat the weeds that compete with crops for nutrients and sunlight [8]. Other common uses of weedicides in the farm are to eradicate invasive plant species or undesirable plants for livestock farms and they can improve production efficiency, facilitate reduced tillage production systems and require fewer costs and human effort [5]. A large number of herbicides have been produced and are currently under development for field crops, and herbicides can be categorized based on their chemical group, application time (preplant, pre- or post-emergence), formulation, mechanism, uptake site, and selectivity [9]. Sulfentrazone, atrazine, isoproturon, and diuron are some of the most widely used herbicides in many countries [10]. Pest control measures can be categorized as mechanical or physical control methods such as tilling, pruning and using screens, fences, and nets. Further biological methods use living organisms (predators, parasites, and herbivorous arthropods) and chemical fights to suppress a pest's density to lower levels [11]. Pesticides are synthetic or natural chemicals used in a variety of agricultural activities to manage plant diseases, weeds, and pests. Herbicides, insecticides, fungicides, and rodenticides are just a few examples of the various pesticides [12]. In the development process of the agricultural industry, pesticides have developed into a crucial tool for protecting plants and increasing agricultural productivity. Because they are inexpensive and effective against a variety of pests, organochlorine insecticides like DDT, hexachlorocyclohexane (HCH), aldrin, and dieldrin are among the most widely used pesticides in developing nations [13]. Conventional weedicides, pesticides, and agrochemicals have become widely used in the agricultural sector, and this has led to a considerable increase in food production and crop yields [14].

1.2 Environmental Issues with Conventional Pesticides and Weedicides

According to previous research, the majority of chemical pesticides used in agriculture have negative effects on the environment and living things that could harm the ecological system. The soil retains a significant portion of the pesticide molecules used in crop fields and for other agricultural purposes. The regular and excessive application of pesticides enhances the issue of soil accumulation [15]. The fate of applied pesticides is determined by some parameters, including soil characteristics and soil microflora, and as a result, it passes through several degradation phases, transportation, and adsorption/desorption mechanisms [16, 17]. Solubility, adsorption, persistence, and volatility are important chemical properties of pesticides. Solubility refers to a pesticide's capacity for dissolving in a solvent, most frequently water. Temperature, pH, substance polarity, size of the pesticide molecule, hydrogen bonds, and the method employed all affect solubility measures. The potential of pesticide molecules to runoff or leach is higher when a pesticide is more water soluble [18]. The low ability of active ingredients to dissolve in water, non-selectivity behavior, and uncontrollable release of active ingredients to the environment are some of the limitations of pesticide formulations [19]. Adsorption causes because the chemical and soil particles are attracted to one another. The organic content and clay particles in the soil are typically more attractive to oil-soluble pesticides than water-soluble pesticides. According to previous findings, the overuse of pesticides reduces the organic matter in the soil, which also affects the soil's capacity to retain water. As a result, the microbial load and variety of the soil decrease, which causes a drop in soil fertility. Furthermore, there is a significant decrease in the overall amount of organic matter in the ground. As a result, droughts are more likely to occur in the area. Therefore, urgent action should be conducted on a global level to address

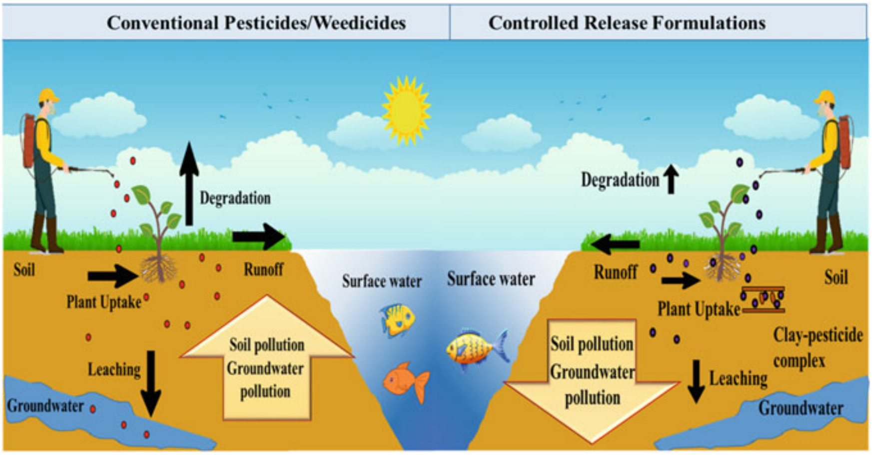


Fig. 1 Environmental benefits of controlled-release formulations over conventional pesticides/ weedicides

the issue of pesticide-related environmental degradation [20]. To reduce the negative consequences of these chemicals, the major health and environmental issues that these toxic substances bring must be controlled as herbicide production and use increase (Fig. 1).

2 Slow-Release Formulations of Weedicides and Pesticides

Due to the rapid release of the active ingredient from commercial formulations, the findings of pesticide controlled/slow-release formulations are a significant concern in the modern agroindustry [12]. There are some advantages of slow-release formulations over conventional formulations including improved pesticide efficacy, increased time of effectiveness of the pesticides, decreased toxicity to non-targeted species, decreased environmental component loss, and preserved the active ingredient. Further, it reduce the surface water and groundwater contamination, less pesticide usage for certain period, and provide safety effect for users. In contrast to conventional pesticides, controlled-release pesticide formulations (CRFs) release pesticide molecules over time, providing for a lesser environmental concentration of the active ingredients while yet maintaining a high level of biological efficacy [21].

Physical or chemical delivery methods are the two main categories for controlled-release pesticides for agrochemicals. In the physical method, the bioactive ingredient is combined with other compounds to prevent its loss by evaporation and leaching, chemical breakdown brought on by the interaction of water, air, and sunshine, or microbiological destruction [22]. In a chemical-controlled release system, an identifiable and distinct chemical bond will be used to chemically bind the agrochemical to a substrate. This would completely remain the agrochemical inactive until it was liberated from the processes like hydrolysis [23]. Matrix systems and reservoir systems are two types of controlled-release systems used in pesticide formulations. The most effective and extensively used method is the matrix system. This involves dissolving or dispersing the agent/pesticide equally throughout the material that has been treated to the necessary shape and geometry. The reservoir-type carriers for controlled-release formulations are frequently made using the microencapsulation technique. Different core materials including, solid type, liquid cores, gas, or a combination of these types, may be included in the design. Similar to this, a variety of materials including biopolymers, inorganic, organic synthetic, and biopolymers and some type of metal oxide could be used to create a protective matrix that was appropriately suited. Natural polymers are typically used as the capping agents in the preparation of formulations for controlled-release pesticides. Natural polymers are favored as pesticide carriers due to their inexpensive cost, free availability, non-toxicity, and biodegradability [24]. In addition to the previously mentioned classifications, numerous groups are working hard to create new and improved formulations for controlled-release pesticides. As an example, the usage of layered double hydroxides (LDH) in controlled release systems is a new trend in the pesticide industry [25].

3 Clay-Based Formulations of Pesticides and Weedicides

Due to their substantial specific surface area, ion-exchange ability, and colloidal characteristics, clays are used in controlled-release systems of pesticides, which has attracted significant interest in both the scientific and industrial fields [26]. Moreover, they have a wide range of applications in agriculture due to the pesticides' reversible adsorption capacity on their surface. The ability of pesticide molecules to undergo photodegradation can have an impact on the active ingredient content present in pesticides used to control weeds and pests. Clays are now being used more frequently in delivery technology to give the active ingredient gradual release qualities [27]. Understanding the various clay-pesticide interactions might be helpful when developing novel pesticide formulations that suit the needs of environmental control. The best pesticide formulation makes sure that the minimum amount of the chemical is released into the environment while still having the maximum effect at the correct time [28]. Pesticides have been released slowly using a variety of clay-based methods, such as changing the surface of the clay by adsorbing organic cations from hydrophilic to hydrophobic, which increases the clay's affinity for hydrophobic herbicides. Other methods include the coagulation of delaminated clay particles to trap the herbicide, sorption on thermally treated clay [29], intercalation of pesticide copolymers, encapsulation within polymer–clay and clay–gel matrixes, etc [30]. The incorporation of clay into pesticide formulations might increase the stability and shelf life of the pesticide products due to its small particle size, high adsorption capacity, ease of surface modification, and unique colloidal properties. Consequently, clays are thought to be a suitable natural inert ingredient for use in creating pesticide formulations [31].

3.1 Types of Clay and Clay Minerals

Clay minerals are categorized as phyllosilicates and predominate in the colloidal fractions of soils, sediments, rocks, and waterways (usually hydrous aluminosilicates). The most prevalent group of sedimentary minerals is clay minerals with a size of less than 2 μm and have a high surface area to mass ratio. Layers of Si–O-tetrahedral and layers of Al or Mg–O–OH octahedral are used to construct clay mineral platelets [32]. Clays exhibit a variety of unique physical, chemical, and physicochemical properties that set them apart from other soil colloids in terms of how they react when interacting with various soil environments (such as cation exchange capacity, specific surface area, porosity, and surface charge characteristics). Naturally, clay is hydrophilic and it is necessary to alter the clay's surface so that hydrophobic polymers can interact with it. Clays have a special property that allows them to exchange cations between each of their layers and retain them. This cation exchange capacity can be defined as the maximum amount of cations that a given amount of clay can take up and this is constant. The cation exchange method is typically used to modify the surface of clay [33]. If dry clay minerals are allowed to adsorb water in a controlled environment, water is added into their interlayer space in more or less discrete forms of layer causing swelling or expansion of the interlayer space. The swelling of the interlayer space of clay minerals is due to the hydration energy forces associated with the interaction of the particles. The swelling clays are prone to large volume changes which are related to changes in water content. As a result, the sheet structure, cation and anion-exchange capacity, and adsorption ability of clay minerals strongly influence their physical and chemical properties, which mostly determine their significance in various applications. Clays can be developed as carriers for pesticide formulation without requiring any modifications. As a pesticide carrier, for instance, raw bentonites have been utilized, and the effectiveness of such formulations depends on the type of bentonite used [31].

Clays or clay minerals are typically modified with surfactants to improve the binding/loading efficiency of the pesticide molecules, such as monomers, micelles, vesicles, polymers, or organic cations and anions. The siloxane surface of clay layers is significantly exposed to adsorb organic substances, including pesticide molecules, when clays are treated with tiny quaternary cations. The modification of the clay surface is generally done by the cation exchange process. Clay can be modified in different ways, and the modified clays are named relevant to the modification method followed [34]. Organoclays are made by substituting organic cations for naturally occurring exchangeable inorganic cations. The surfaces of the clay are significantly altered and turn organophilic when the interlayer metal cations are switched out for organic cations. Thermal modification of the clays can modify their chemical and mineralogical makeup. Clays are gradually heated to remove structural, adsorbed, and free water. At temperatures higher than 400 °C, irreversible dehydration occurs. Another method of modifying clay is acid treatment, which is mostly employed to enhance the catalytic characteristics of minerals. Since the nature of the clay minerals' surfaces determines their adsorptive and catalytic behavior, an acid treatment will result in the change of original active sites. Clay nanocomposites modify over a nanometer scale in composition and structure. The clay nanolayer needs to be evenly spread (exfoliated) in the polymer matrix to produce real nanocomposites. Natural clays like montmorillonite, hectorite, sepiolite, laponite, saponite, rectorite, bentonite, vermiculite, beidellite, kaolinite, and chlorite as well as synthetic clays like different layered double hydroxides, synthetic montmorillonite, synthetic hectorite, etc., are among the modified clays used in composite preparation [35].

The design and creation of pesticide formulations can benefit from the high sorption capacities and colloidal characteristics of clays and clay minerals. In some pesticides' slow-release formulations (SRFs), clay minerals have been considered suitable formulates. To prevent pesticide leaching, two broad strategies for formulations of pesticides with slow release were developed: (1) using organoclays, and (2) using micelle-, liposome-, and polymer–clay minerals [36]. Other approaches formulations for insecticides and pesticides are frequently created using biodegradable components. In the development of pesticide formulations, substances such as synthetic polymers (polyvinyl alcohol), modified biopolymers, starch, pectin, cellulose-like polysaccharides and proteins, polyesters, shellack, resins, lignin, sporopollenin, latex, and are utilized. These substances also come from plants, animals, and microbes. In these formulations, to improve the gradual release of the active ingredient, clays can be blended into the matrix like modifiers [37]. Clays are commonly utilized as adsorbents for cationic and highly polar pesticides because they are hydrophilic and have a negative charge on their surface, however they exhibit less adsorption for extremely hydrophobic and anionic pesticides. Since cationic pesticides have a great potential to bind to clay minerals and colloidal soil particles, leaching of these substances is rarely a concern. Initially, the development of organoclays was focused on improving the adhesion of hydrophobic pesticides and neutral formulations by delaying their release. The clay mineral surface changes from being hydrophilic to hydrophobic as a result of the adsorption of organic cations. The improved clay mineral surface may have improved potential for adsorbing hydrophobic neutral organic compounds [38]. The most crucial reaction to alter the adsorbent and get the best possible interaction between the pesticide and clay mineral is cation exchange with the type of organic cations. Another type of organoclay occurs when the loading of the organic cations exceeds the cation exchange capacity of the clay mineral, which becomes positively charged and potentially suitable for the adsorption of anions, such as imazaquin [39].

Most pesticide compounds contain polar functional groups such as hydroxyl, chloride, and nitrite which are bound together by dipole-ion or coordination-type interactions. Direct formation of coordination bonds between the adsorptive and the cation or the use of water molecules as bridging ligands are also possible. Regarding base adsorption, whether the ligand is directly coupled to the metal ions or through water molecules is indicated by the concepts of hard and soft acids and bases. Because it affects the base character of the surface, the oxidation state of structural iron can also have an impact on the adsorption of pesticides [28]. Ion exchange mechanisms cause some cationic insecticides to be absorbed by clay minerals. The water molecules and counterions (at the clay's exchangeable sites) also act as a link between the two layers, keeping them constrained. Anionic pesticides can bind with clay minerals on the positively charged clay lamellae edges or at the cation bridges of exchange sites with particular multivalent metal ions [25]. The granules, baits, and dust in some of the microbial pesticide formulations currently in use are clay mineral-based transporters that convey the toxin to the pest's feeding site [40]. The ability of pesticide molecules to undergo photodegradation can have an impact on the amount of the active component used in pesticides to control weeds and pests. Further, the pesticide molecule can be photoexcited and reverted to its ground state before photodecomposition takes place by using an organic cation adsorbed on the clay mineral as an energy acceptor. This causes the pesticide to become photostabilized [27]. The variety of interactions between pesticides and clay serves as the basis for efforts to decrease the harmful spread of these substances in the environment. Clays are therefore considered to be a useful natural inert component for use in developing pesticide formulations. According to current research, these modifications are necessary to maintain agricultural sustainability over the long term.

3.2 Nanomaterial-Based Clay Composites

After the improvement of nanomaterials and nanotechnology, the creation of controlled and slow-release pesticides has moved to the use of nano-pesticides. Nanomaterials have different physical and chemical characteristics from macroscopic materials. To enhance the adsorption and slow release of neutral and hydrophobic active substances, clay-based nanoformulations have been developed. Nanoclays, also known as clay-based nanoformulations, are thin silicate sheets with a 1 nm thickness and a 70–150 nm width, like the montmorillonite clays that are frequently found in volcanic ash. Clay minerals known as nanoclays have at least one dimension that is in the nanometric range. They mostly belong to phyllosilicates and are found in a wide range of clay minerals. As layered aluminosilicates, phyllosilicates are made up of layers of silicon oxide and aluminium sheets placed on top of one another. These structures, which make up the fundamental structural component of nanoclays, can be made up of two, three, or even four layers of silicon tetrahedra, aluminum octahedra layers [41]. In order to provide clay nanoparticles useful properties, modification has been done to them (e.g., large surface area, charge density, hydrophilic nature, and porosity) [42]. The physical and chemical structure of nanoclays are used in the modification processes to create physical or chemical bonds with a variety of substances that fit in the galleries or are held at the sheet edges. These have been created to improve the regulated release and adsorption of active substances that are neutral and hydrophobic. The type of interaction between a pesticide and nanoclay will depend on the chemical characteristics of the material being hosted. Hydrogen bonds, dipole–dipole interactions, ion–dipole, covalent bonding, ionic couples, ion-pi interactions, and cation exchange are a few examples of possible bond types [43]. Due to their potential use as nanocarriers in agricultural and materials science applications, nanoclays are seen as being a commercially viable and biocompatible material that can offer better prospects [12]. Clay-based materials have been proven as an innovative approach for eco-friendly active ingredient delivery systems. Researchers have been driven to develop nanopesticides that are more target-specific and less hazardous to the environment by the rapid advancements in pesticide research [24].

Nanoclays carrying active plant protection substances are used for similar reasons as in growth promotion but are related to the pesticidal activity. Clay nanotubes were created as inexpensive pesticide delivery systems. They improve pesticide effectiveness, decrease the number of pesticides used, have a longer release period and better plant contact, reduce pesticide leaching and residues, and do so with the least amount of environmental damage [44]. The encapsulation and trapping via weak ionic attachments, among other methods, have enabled slow and steady distribution [45]. These mechanisms not only provide a cushion against environmental degradation but also reduce the cost of application as a small amount is required due to efficient absorption [46]. Several parameters can affect the intercalation of active ingredients inside clay such as spacing and the presence of water molecules between interlayers and exchangeable cations. Nanoclay gutbusters are a different class of functional nanoinsecticide that work when exposed to an alkaline environment, such as the stomach of an insect. In addition to nanoclay insecticides, emerging pesticide technologies include nanoclay herbicides, growth regulators, fungicides, and nanosensors for pesticide and plant pathogen detection. Moreover, the environmental concerns related to chemical runoff are also reduced which ensures environmental stability. For the protection of insecticides against extreme environmental conditions, nanocarriers are very helpful [36]. The modification of clay with organic cations helped to enhance their affinity for the adsorption of hydrophobic active ingredients such as alachlor, acetochlor, metolachlor, and metolachlor norflurazon [27]. In the future, there should be a focus on understanding the molecular and conformation mechanisms involved with the delivery of pesticides to the structural modification of nanoscale carriers involved (Table 1).

3.3 Controlled Release Mechanisms of Clay-Based Pesticide Formulations

Most of the systems currently in use are based on more controllable mechanisms, like diffusion through rate-controlling media, erosion of biodegradable barrier materials, and retrograde chemical reactions, although the first formulations relied on the

Table 1 Clay-based slow-release formulations of different weedicides and pesticides

Clay-based formulation	Active ingredient	Attributes	Effective against	References
Starch–alginate and bentonite clay-based formulation	Thiram (dithiocarbamate)	Controlled release	Fungal diseases	[26]
Bentonite-polymer composite	Metribuzin	Slow release	Weeds	[47]
Sepiolite	Mesotrione	Slow release and reduced leaching losses	Weeds	[48]
Bentonite and Activated Carbon	Carbofuran	Slow release	Insects and nematodes	[49]
Methoxy-modified Kaolinite	3-Amino-1,2,4-triazole, (amitrole)	High-capacity loading and controlled release	Weeds	[50]
Montmorillonite phosphatidylcholine	Diuron	Reduced leaching losses	Weeds	[51]
Micelles adsorbed on Montmorillonite	Sulfosulfuron	Reduced leaching and enhanced biological activity	Weeds	[52]
Organo-clay formulations of montmorillonite/ sepiolite	Norflurazon	Enhanced adsorption and reduced leaching	Weeds	[53]
Bentonite clay hydrogels composite	Thiamethoxam	Slow release	Insects	[54]
Carboxymethyl starch/ montmorillonite composite	Isoproturon	Reduced the potential leaching	weeds	[55]
Bentonite, montmorilloniteiron oxide, kaolinite	Atrazine and Alachlor	Controlled release	Weeds	[56]
Alginate/exfoliated montmorillonite nanocomposite	Acetamiprid	Slow and sustained release	Insects	[57]

pesticides' desorption from powerful sorbents including silica, mica, and activated charcoal. Understanding the technique by which a molecule of pesticide is essential for a controlled or slow release to be effectively transported from starting location to the exterior within a matrix and then how it will be released to the environment in a gradual or regulated pattern [22].

(a) **Diffusion-Controlled Release**

Diffusion is often the primary release mechanism that takes place through water-filled pores and relies on the matrix's porous nature and polymeric covering. The agent is contained by the matrix's biodegradable and non-biodegradable components. The active compound was delivered by migration and diffusion inside the reservoir matrix surface, followed by delivery to the medium from the surface in the space between the matrix and the surrounding medium. The pesticide molecule must be connected to the exterior surface by a series of pores in the matrix, each of which contains enough space to accommodate the pesticide molecule. The active ingredient shifts towards the surface through the water-filled pores in the coating layer, creating a reservoir of the active ingredient. This process takes some time and results in a prolonged release. The thickness of the membrane, the solubility of the active ingredient in water, and the surroundings are a few of the aspects that influence the outflow of the active ingredient once again.

(b) **Solvent-activated release due to osmotic pressure**

The second possible mechanism, known as solvent-controlled release, is based on the phenomenon known as "osmosis," which is described as the total flow of water over a selective membrane that is regulated by the pressure gradient across the membrane. Some materials may be affected by changes in hydrophobicity and changed interactions between organic groups and show swelling or shrinking in water [58]. The structural chains that support the diffusion and release of the pesticide molecules are moved more rapidly as a result of these processes. Due to the pressure gradient that has formed, the pesticide molecule moves outside of this area. The diffusion coefficient of the active ingredient and the relaxation of the polymeric chain backbone both affect the release [59]. Since they raise the hydrostatic pressure due to their swelling nature, water-absorbing matrices are employed for insecticides that are only weakly water-soluble. Osmotically controlled release, when it comes to delivering insoluble chemicals, osmotic techniques show promise. The active substance, which is distributed in a polymeric matrix and is unable to permeate through it, can be ejected more easily due to osmotic pressure.

(c) **Stimulus-responsive release**

Materials that are intelligent and able to change their behavior in response to changes in environmental parameters have the potential for controlled release. To improve the controlled release system, formulations using stimuli-sensitive carriers are designed. In this system, macromolecules respond actively to minute signals or alterations in their environment, which causes changes in their physicochemical properties that favor the release of loaded substances [60].

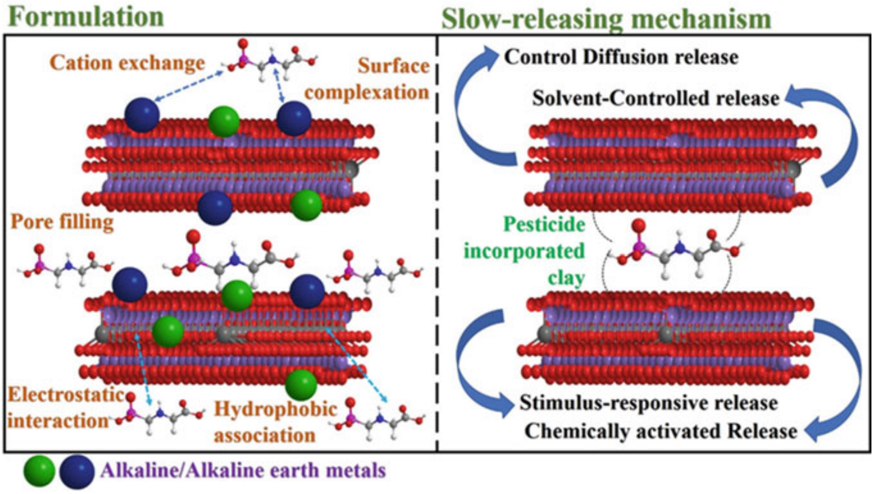


Fig. 2 Different clay–pesticides interactions and releasing mechanisms

These sensitive carriers can enable the release of active chemicals in response to abiotic or biotic stimuli including light, pH, temperature, magnetic field, and enzymes, among others, when utilized in agrochemical formulations [61]. Due to their widespread availability and biodegradability, natural polymers (including alginate, cyclodextrin, starch, chitosan, carboxymethylcellulose, and ethylcellulose) and silicas can be used to create stimuli-controlled delivery systems [62].

(d) Chemically activated Release

The ester, amide, and hydrazone linkages in the backbones of biodegradable polymers such as polyesters, polyamides, poly (amino acids), and polysaccharides that were employed in different controlled or slow-release formulations are anticipated to release active ingredients by hydrolytic and/or enzymatic decomposition. The process of degradation, which is regarded as the rate-determining step, regulates the progression of diffusion during the last phase of pesticide release. Chemical combinations have the pesticide securely connected to the polymeric substrate by a distinct, observable chemical bond, as opposed to physical combinations where the pesticide is dissolved or trapped in polymers [63] (Fig. 2).

4 Emerging Challenges and Future Perspectives

The development of ecologically safe herbicide/pesticide formulations can be considered one of the major aspects of sustainable agriculture. Keeping the biological effectiveness of the pesticide active ingredient included in the matrix is one of the difficulties in designing slow-release pesticide formulations using clay composites.

To effectively control weeds, clay based slow-release herbicide formulations must be developed as well as their biological activity in comparison to the herbicidal activity of the free active chemical studied [64]. Leaching of the active substance from these regulated clay based formulations is another topic that is not fully explored. It is well established that one of the main adverse effects of pesticide use is leaching, which results in anthropogenic issues including soil and groundwater pollution. Leaching study of the slow-release formulations of pesticides in soil should also be taken into consideration [65]. The high amount of pesticide that is not released from many clay-pesticide formulations that have been assayed as a major barrier. This would cause soil contamination and necessarily require using greater amounts of the formulation, significantly increasing application rates, to release the same amount of active ingredient. It is important to consider the factors that influence the rate and degree of pesticide release from clays and organoclays in order to overcome the mentioned interferences [66]. The clay-pesticide ratio, the number and type of exchangeable cations, the clay mineral's properties, and the procedures taken to develop the formulation all have an impact on how the pesticide interacts with the sorbent, which in turn affects the formulation's release rate and extent [67]. While the variety of organoclay-pesticide interactions has received a lot of attention, there is insufficient information available on the variables affecting the rate and extent of pesticide release from organoclay formulations. Studies that assess the way how organoclay formulations of pesticides behave in actual field settings are relatively limited, however the comparable or even improved weed control efficacy reported by several authors for these formulations when compared to standard formulations appear encouraging for their practical use [24]. Clay minerals are naturally occurring nanomaterials that can be altered to improve interactions between the active ingredients and the resulting matrix. This results in a delivery system that gradually releases the active ingredient close to the target, reducing losses of the bioactive compound while maintaining bioefficacy. To screen and validate the eco safe formulations, the initial evaluations must be carried out under gnotobiotic or controlled environmental settings [48]. Despite these developments in nanocarrier applications, crystalline impurities in clay nanoparticles continue to be a significant problem. To improve their use in pesticide delivery, effective synthesis processes and appropriate surface modification techniques must be developed. A more practical method for assessing the advantages of nanobased agricultural applications such as effectiveness, cost-effectiveness, and impact on the environment would be large-scale field tests of new nanoagrochemicals in comparison to their conventional counterparts.

Acknowledgements Financial assistance by RG/2021/AG/02 grant received from the National Science Foundation, Sri Lanka

References

1. Bajwa, A.A.: Sustainable weed management in conservation agriculture. J. Crop Prot. **65**, 105–113 (2014)
2. Zhila, N., Murueva, A., Shershneva, A., Shishatskaya, E., and Volova, T.: Herbicidal activity of slow-release herbicide formulations in wheat stands infested by weeds. J. Environ. Sci. Health B. **52**(10), 729–735 (2017)
3. Waterfield, G., Zilberman, D.: Pest management in food systems: an economic perspective. Annu. Rev. Environ. Resour. **37**, 223–245 (2012)
4. Fand, B.B., Kamble, A.L., Kumar, M.: Will climate change pose serious threat to crop pest management: a critical review. Int. J. Sci. Res. Publ. **2**(11), 1–14 (2012)
5. Monteiro, A., Santos, S.: Sustainable approach to weed management: the role of precision weed management. Agron. **12**(1), 118 (2022)
6. Scavo, A., Mauromicale, G.: Integrated weed management in herbaceous field crops. Agron. **10**(4), 466 (2020)
7. Talaviya, T., Shah, D., Patel, N., Yagnik, H., Shah, M.: Implementation of artificial intelligence in agriculture for optimisation of irrigation and application of pesticides and herbicides. Artif. Intell. Agric. **4**, 58–73 (2020)
8. Varshney, S., Hayat, S., Alyemeni, M.N., Ahmad, A.: Effects of herbicide applications in wheat fields: is phytohormones application a remedy?Plant Signal. Behav. **7**(5), 570–575 (2012)
9. Sherwani, S.I., Arif, I.A., and Khan, H.A.: Modes of action of different classes of herbicides. Herbicides, Physiology of Action, and Safety. 2015: InTech Publishers Croácia, 165–186
10. Vonk, J.A. and Kraak, M.H.S.: Herbicide exposure and toxicity to aquatic primary producers. In: Reviews of Environmental Contamination and Toxicology, vol. 250, 119–171 pp. Springer (2020)
11. Bradford, K.J., Dahal, P., Van Asbrouck, J., Kunusoth, K., Bello, P., Thompson, J., and Wu, F.: The dry chain: reducing postharvest losses and improving food safety in humid climates. In: Food Industry Wastes, 375–389 pp. Elsevier (2020)
12. Kumar, S., Nehra, M., Dilbaghi, N., Marrazza, G., Hassan, A.A., and Kim, K.-H.: Nano-based smart pesticide formulations: emerging opportunities for agriculture. JCR **294**, 131–153 (2019)
13. Abhilash, P.C. and Singh, N.: Pesticide use and application: an Indian scenario. J. Hazard. Mater. **165**(1–3), 1–12 (2009)
14. Linquist, B.A., Liu, L., van Kessel, C., and van Groenigen, K.J.: Enhanced efficiency nitrogen fertilizers for rice systems: meta-analysis of yield and nitrogen uptake. Field Crops Res. **154**, 246–254 (2013)
15. Sharma, N., Singhvi, R.: Effects of chemical fertilizers and pesticides on human health and environment: a review. Int. J. Agric. Environ. Biotechnol. **10**(6), 675–680 (2017)
16. Weber, J.B., Wilkerson, G.G., Reinhardt, C.F.: Calculating pesticide sorption coefficients (Kd) using selected soil properties. Chemosphere **55**(2), 157–166 (2004)
17. Hussain, S., Siddique, T., Saleem, M., Arshad, M., Khalid, A.: Impact of pesticides on soil microbial diversity, enzymes, and biochemical reactions. Adv. Agron. **102**, 159–200 (2009)
18. Wauchope, R.D., Yeh, S., Linders, J.B.H.J., Kloskowski, R., Tanaka, K., Rubin, B., Katayama, A., Kördel, W., Gerstl, Z., and Lane, M.: Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. Pest Manag. Sci. **58**(5), 419–445 (2002)
19. Grant, S., Mortimer, M., Stevenson, G., Malcolm, D., Gaus, C.: Facilitated transport of dioxins in soil following unintentional release of pesticide-surfactant formulations. Environ. Sci. Technol. **45**(2), 406–411 (2011)
20. Sharma, A., Shukla, A., Attri, K., Kumar, M., Kumar, P., Suttee, A., Singh, G., Barnwal, R.P., Singla, N.: Global trends in pesticides: a looming threat and viable alternatives. Ecotoxicol. Environ. Saf. **201**, 110812 (2020)
21. Garrido-Herrera, F.J., Gonzalez-Pradas, E., and Fernández-Pérez, M.: Controlled release of isoproturon, imidacloprid, and cyromazine from alginate–bentonite-activated carbon formulations. J. Agric. Food Chem. **54**(26), 10053–10060 (2006)

22. Ashitha, A. and Mathew, J.: Characteristics and types of slow/controlled release of pesticides. In: Controlled release of pesticides for sustainable agriculture, 141–153 pp. Springer (2020)
23. Ortiz-Hernández, M.L., Sánchez-Salinas, E., Dantán-González, E., Castrejón-Godínez, M.L.: Pesticide biodegradation: mechanisms, genetics and strategies to enhance the process. Biodegrad.-Life Sci. **10**, 251–287 (2013)
24. Singh, A., Dhiman, N., Kar, A.K., Singh, D., Purohit, M.P., Ghosh, D., and Patnaik, S.: Advances in controlled release pesticide formulations: Prospects to safer integrated pest management and sustainable agriculture. J. Hazard. Mater. **385**, 121525 (2020)
25. Cornejo, J., Celis, R., Pavlovic, I., and Ulibarri, M.A.: Interactions of pesticides with clays and layered double hydroxides: a review. Clay Minerals **43**(2), 155–175 (2008)
26. Singh, B., Sharma, D.K., Kumar, R., Gupta, A.: Controlled release of the fungicide thiram from starch–alginate–clay based formulation. Appl. Clay Sci. **45**(1–2), 76–82 (2009)
27. El-Nahhal, Y., Undabeytia, T., Polubesova, T., Mishael, Y.G., Nir, S., Rubin, B.: Organo-clay formulations of pesticides: reduced leaching and photodegradation. Appl. Clay Sci. **18**(5–6), 309–326 (2001)
28. Lagaly, G.: Pesticide–clay interactions and formulations. Appl. Clay Sci. **18**(5–6), 205–209 (2001)
29. Bojemueller, E., Nennemann, A., Lagaly, G.: Enhanced pesticide adsorption by thermally modified bentonites. Appl. Clay Sci. **18**(5–6), 277–284 (2001)
30. Maqueda, C., Villaverde, J., Sopeña, F.t., Undabeytia, T.s., and Morillo, E.: Novel system for reducing leaching of the herbicide metribuzin using clay–gel-based formulations. J. Agric. Food Chem. **56**(24), 11941–11946 (2008)
31. Singh, G., Ramadass, K., Sooriyakumar, P., Hettithanthri, O., Vithange, M., Bolan, N., Tavakkoli, E., Van Zwieten, L., and Vinu, A.: Nanoporous materials for pesticide formulation and delivery in the agricultural sector. JCR 343, 187–206 (2022). https://doi.org/10.1016/j.jconrel.2022.01.036
32. Kumari, N., Mohan, C.: Basics of clay minerals and their characteristic properties. Clays Clay Miner. **24**, 1–29 (2021). http://dx.doi.org/https://doi.org/10.5772/intechopen.97672
33. Kozak, M. and Domka, L.: Adsorption of the quaternary ammonium salts on montmorillonite. J. Phys. Chem. Solids **65**(2–3), 441–445 (2004)
34. Basak, B.B., Pal, S., Datta, S.C.: Use of modified clays for retention and supply of water and nutrients. Curr. Sci. **102**(9), 1272–1278 (2012)
35. Kotal, M., Bhowmick, A.K.: Polymer nanocomposites from modified clays: recent advances and challenges. Prog. Polym. Sci. **51**, 127–187 (2015)
36. Nuruzzaman, M.D., Rahman, M.M., Liu, Y., and Naidu, R.: Nanoencapsulation, nano-guard for pesticides: a new window for safe application. J. Agric. Food Chem. **64**(7), 1447–1483 (2016)
37. Zhao, R., Torley, P., and Halley, P.J.: Emerging biodegradable materials: starch-and protein-based bio-nanocomposites. J. Mater. Sci. **43**(9), 3058–3071 (2008)
38. Nir, S., El-Nahhal, Y., Undabeytia, T., Rytwo, G., Polubesova, T., Mishael, Y., Rabinovitz, O., and Rubin, B.: Clays, clay minerals, and pesticides. In Developments in Clay Science, Vol. 5, 645–662 pp. Elsevier (2013)
39. Nir, S., El Nahhal, Y., Undabeytia, T., Rytwo, G., Polubesova, T., Mishael, Y., Rabinovitz, U., and Rubin, B.: Clays and pesticides. Dev. Clay Sci. **1**, 677–691 (2006)
40. Ansari, I., El-Kady, M.M., Arora, C., Sundararajan, M., Maiti, D., and Khan, A.: A review on the fatal impact of pesticide toxicity on environment and human health. Global Climate Change 361–391 (2021)
41. Nazir, M.S., Mohamad Kassim, M.H., Mohapatra, L., Gilani, M.A., Raza, M.R., and Majeed, K.: Characteristic properties of nanoclays and characterization of nanoparticulates and nanocomposites. In: Nanoclay Reinforced Polymer Composites, 35–55 pp. Springer (2016)
42. Konappa, N., Krishnamurthy, S., Arakere, U.C., Chowdappa, S., Akbarbasha, R., Ramachandrappa, N.S.: Nanofertilizers and nanopesticides: recent trends, future prospects in agriculture. In: Advances in Nano-Fertilizers and Nano-Pesticides in Agriculture, 281–330 pp. Elsevier (2021)

43. Jayrajsinh, S., Shankar, G., Agrawal, Y.K., and Bakre, L.: Montmorillonite nanoclay as a multifaceted drug-delivery carrier: a review. J. Drug Deliv. Sci. Technol. **39**, 200–209 (2017)
44. Constantinescu, F., Sicuia, O.A.B.: Phytonanotechnology and plant protection. In: Phytonanotechnology, 245–287 pp. Elsevier (2020)
45. Ditta, A. Role of nanoclay polymers in agriculture: Applications and perspectives. In Nanohybrids in Environmental & Biomedical Applications, pp. 323–334. CRC Press (2019)
46. Fei Guo, C., Sun, T., Cao, F., Liu, Q., and Ren, Z.: Metallic nanostructures for light trapping in energy-harvesting devices. Light Sci. Appl. **3**(4), e161 (2014)
47. Sahoo, S., Manjaiah, K.M., Datta, S.C., Ahmed Shabeer, T.P., Kumar, J.: Kinetics of metribuzin release from bentonite-polymer composites in water. J. Environ. Sci. Health B. **49**(8), 591–600 (2014)
48. del Carmen Galán-Jiménez, M., Morillo, E., Bonnemoy, F., Mallet, C., Undabeytia, T.: A sepiolite-based formulation for slow release of the herbicide mesotrione. Appl. Clay Sci. **189**, 105503 (2020)
49. Fernández-Pérez, M., Villafranca-Sánchez, M., Flores-Céspedes, F., Garrido-Herrera, F.J., and Pérez-García, S.: Use of bentonite and activated carbon in controlled release formulations of carbofuran. J. Agric. Food Chem. **53**(17), 6697–6703 (2005)
50. Tan, D., Yuan, P., Annabi-Bergaya, F., Liu, D., He, H.: Methoxy-modified kaolinite as a novel carrier for high-capacity loading and controlled-release of the herbicide amitrole. Sci. Rep. **5**(1), 1–6 (2015)
51. Undabeytia, T., Recio, E., Maqueda, C., Sánchez-Verdejo, T., Balek, V.: Slow diuron release formulations based on clay–phosphatidylcholine complexes. Appl. Clay Sci. **55**, 53–61 (2012)
52. Mishael, Y.G., Undabeytia, T., Rabinovitz, O., Rubin, B., and Nir, S.: Sulfosulfuron incorporated in micelles adsorbed on montmorillonite for slow release formulations. J. Agric. Food Chem. **51**(8), 2253–2259 (2003)
53. Undabeytia, T., Nir, S., and Rubin, B.: Organo-clay formulations of the hydrophobic herbicide norflurazon yield reduced leaching. J. Agric. Food Chem. **48**(10), 4767–4773 (2000)
54. Sarkar, D.J., Singh, A.: Base triggered release of insecticide from bentonite reinforced citric acid crosslinked carboxymethyl cellulose hydrogel composites. Carbohydr. Polym. **156**, 303–311 (2017)
55. Wilpiszewska, K., Spychaj, T., Paździoch, W.: Carboxymethyl starch/montmorillonite composite microparticles: properties and controlled release of isoproturon. Carbohydr. Polym. **136**, 101–106 (2016)
56. Johnson, R.M., Pepperman, A.B.: Release of atrazine and alachlor from clay-oxamide controlled-release formulations. Pestic. Sci. **53**(3), 233–240 (1998)
57. Yan, H., Chen, X., Feng, Y., Xiang, F., Li, J., Shi, Z., Wang, X., Lin, Q.: Modification of montmorillonite by ball-milling method for immobilization and delivery of acetamiprid based on alginate/exfoliated montmorillonite nanocomposite. Polym. Bull. **73**(4), 1185–1206 (2016)
58. Cath, T.Y., Childress, A.E., and Elimelech, M.: Forward osmosis: Principles, applications, and recent developments. J. Membr. Sci. **281**(1–2), 70–87 (2006)
59. Peppas, N.A., Bures, P., Leobandung, W.S., Ichikawa, H.: Hydrogels in pharmaceutical formulations. Eur. J. Pharm. Biopharm. **50**(1), 27–46 (2000)
60. Camara, M.C., Campos, E.V.R., Monteiro, R.A., do Espirito Santo Pereira, A., de Freitas Proença, P.L., Fraceto, L.F.: Development of stimuli-responsive nano-based pesticides: emerging opportunities for agriculture. J. Nanobiotechnology. **17**(1), 1–19 (2019)
61. Goponenko, A.V., Dzenis, Y.A.: Role of mechanical factors in applications of stimuli-responsive polymer gels–Status and prospects. Polymer **101**, 415–449 (2016)
62. Neri-Badang, M.C. and Chakraborty, S.: Carbohydrate polymers as controlled release devices for pesticides. J. Carbohydr. Chem. **38**(1), 67–85 (2019)
63. Li, N., Sun, C., Jiang, J., Wang, A., Wang, C., Shen, Y., Huang, B., An, C., Cui, B., Zhao, X.: Advances in controlled-release pesticide formulations with improved efficacy and targetability. J. Agric. Food Chem. **69**(43), 12579–12597 (2021)
64. Volova, T., Shumilova, A., Zhila, N., Sukovatyi, A., Shishatskaya, E., Thomas, S.: Efficacy of slow-release formulations of metribuzin and tribenuron methyl herbicides for controlling weeds of various species in wheat and barley stands. ACS Omega **5**(39), 25135–25147 (2020)

65. Aktar, W., Sengupta, D., Chowdhury, A.: Impact of pesticides use in agriculture: their benefits and hazards. Interdiscip. Toxicol. **2**(1), 1–12 (2009)
66. Lagaly, G.: Pesticide–clay interactions and formulations. Appl. Clay Sci. **18**(5–6), 205–209 (2001)
67. Nennemann, A., Mishael, Y., Nir, S., Rubin, B., Polubesova, T., Bergaya, F.z., van Damme, H., Lagaly, G.: Clay-based formulations of metolachlor with reduced leaching. Appl. Clay Sci. **18**(5–6), 265–275 (2001)
68. Galán-Jiménez, M.d.C., Mishael, Y.-G., Nir, S., Morillo, E., and Undabeytia, T.: Factors affecting the design of slow release formulations of herbicides based on clay-surfactant systems. A methodological approach. Plos one **8**(3), e59060 (2013)
69. Sharma, B., Lakra, U., Sharma, R., and Sharma, S.R.: A comprehensive review on nanopesticides and nanofertilizers—A boon for agriculture. Nano-Enabled Agrochem. Agric. 273–290 (2022)
70. Kalia, A., Sharma, S.P., Kaur, H., Kaur, H.: Novel nanocomposite-based controlled-release fertilizer and pesticide formulations: Prospects and challenges. In: Multifunctional Hybrid Nanomaterials for Sustainable Agri-food and Ecosystems, 99–134 pp. Elsevier (2020)

Clay Hybrids for Sustained-Release Fertilizer

Randima Edussuriya, Anushka Upamali Rajapaksha, and Meththika Vithanage

Abstract Conventional chemical fertilizers immediately release the majority of their nutrient content after applying it to the soil. Therefore, a significant amount of the released nutrients cannot be utilized by the crops. Excess amounts of nutrients can undergo hydrolysis and microbial action, posing a possible threat to the environment by facilitating and releasing hazardous compounds. When compared with conventional fertilizers, controlled nutrient release is thought to be an effective strategy to fulfill the nutrient demand of crops throughout the growth period. Fertilizer treated with clay composites also has slow-release properties. Clay minerals' hydrous layer aluminosilicates constitute the greater part of the phyllosilicates. The use of nanoclay-polymer composites, one of the more recent fertilizer delivery alternatives, may open up new opportunities for managing an effective supply of nutrients. Clay composites' barrier properties are increased when the clay is modified with polymers, especially surface crosslinking polymers. Therefore, this chapter stated the mechanism, developments, and future potential of clay-based hybrid fertilizer formulations that ensure the long-term sustainability of agricultural management systems.

Keywords Slow-release formulations · Coated fertilizer · Hybrid nanocomposites · Modified clay

---

R. Edussuriya · A. U. Rajapaksha · M. Vithanage (✉)
Ecosphere Resilience Research Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, 10250 Nugegoda, Sri Lanka
e-mail: meththika@sjp.ac.lk

A. U. Rajapaksha
Instrument Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, 10250 Nugegoda, Sri Lanka

M. Vithanage
Sustainability Cluster, School of Engineering, University of Petroleum & Energy Studies, Dehradun, Uttarakhand 248007, India

Institute of Agriculture, University of Western Australia, Perth WA6009, Australia

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_25

1 Fertilizer, Agriculture, and the Environment

Crop production has to be improved, expanded, and secured globally to prevent shortages given the world's growing population. However, the increase in agricultural operations over the past decades has caused environmental distress including climate change, depletion of natural resources, and shortage of energy, which has put a significant strain on the sustainability and steady supply of food [1]. Both organic and inorganic fertilizers have been used for years to meet the rising demand for agricultural products [2]. Excessive use of fertilizer considerably reduces the effectiveness of fertilizer use and results in significant environmental and ecological problems [3]. Chemical or inorganic fertilizers contain one or more nutrient mineral elements required for crop [4]. It has been widely accepted that using excessive amounts of inorganic fertilizers, particularly nitrogen, has the potential to degrade the soil environment and can also result in the mineralization of organic matter. Therefore, using chemical or inorganic fertilizers to increase agricultural yield and soil fertility is not a sustainable approach [5]. Fertilizer application that is excessive or out of control degrades soil qualities including osmolarity and water-holding capacity. Additionally, excessive use can harm soil microbes [6].

Excess amounts of nutrients can undergo hydrolysis and microbial action while it could be a potential threat to the environment by accelerating the water eutrophication and emission of hazardous compounds [7]. Organic fertilizers contain livestock waste including litter, animal manure and residue, sewage and agricultural waste. The origin and chemical characteristics affect the effect of organic fertilizer [8]. Direct application of animal manure to the field or soil may lead to over-fertilization due to uncontrollable nutrient release and excessive use of organic fertilizer [9]. Also it may result in the release of pollutant gases including CO_2, CH_4 and spread of harmful pathogens to the soil [10]. These effects cause a substantial economic downturn, major environmental problems, such as soil, freshwater, and ocean pollution, as well as a reduction in farming biodiversity [11]. The conventional fertilizer should be enhanced by changing the ability to lower the fertilizer loss, increasing the soil nutrient retention, and improving fertilizer utilization efficiency. Consequently, these modifications are expected to enhance agricultural productivity and significantly minimize the negative environmental effects caused by the excessive and inappropriate use of fertilizers.

2 Controlled-Release Fertilizer

The efficiency of nutrient delivery with higher nutrient usage and less environmental pollution determine by two things: Keeping nutrient availability and matching the supplement of nutrients with plant demand. Introduction of controlled-release fertilizers (CRFs) is one efficient way to improve nutrient use efficiency and reduce environmental impacts [12]. Compared to quick release fertilizers, controlled-release fertilizers offer a longer nutrient delivery. As a result of controlled release of nutrients into the fixing media throughout the process of fixation in the soil, controlled-release fertilizers enhanced the availability of nutrients [13]. Controlled-release fertilizers are mostly made from organic source materials that are naturally occurring, like animal waste or sewage sludge, they may also be made from synthetic organic compounds with nitrogen that have a low solubility (urea formaldehyde) [14]. Generally applied soluble inorganic fertilizers may classify as CRFs if they contain a physical barrier that regulates the release of nutrients. Such a barrier can be created by utilizing a hydrophobic material matrix or covering the fertilizer with a hydrophobic polymer surface [15]. There are several economical, agricultural, and environmental aspects of using CRFs. Controlled-release fertilizer can be applied to soils in place of conventional fertilizers and has an effective nutrition loading capacity, storage, and proper nutrient utilization. In addition to the benefits to the environment, their one application lowers the labor and energy expenses associated with the repeated applications of conventional fertilizers [13]. In-depth research has been done on controlled-release fertilizers (CRFs), which offer a safer, more cost-effective, and effective way to give nutrients since they are made as more available to the target species at the appropriate rate or concentration level, keeping the nutrients in the soil for a longer time [16].

2.1 Classification of Controlled/Slow-Release Fertilizer

Physical and chemical types of fertilizers comprise the majority of slow/control fertilizers used today, and the use of compound-type SRF/CRF has very incidentally been documented. Physical type belonging to SRF by using coating forms or matrix to control the speed at which soil water enters the fertilizer core and nutrient solution from the inside out. It is further separated into matrix fertilizers and coated fertilizers (Fig. 1). Early on, this type of fertilizer was widely used, and also it has uneven slow-release characteristics. In order to create a compact, low permeability film on the surface of the fertilizer particles, coated fertilizer is created by spraying one or more layers of inert material over the surface of the fertilizer particles [14]. Different slow-release effects are produced by the membrane structure's various features. The most popular coated slow-release fertilizers are urea coated with sulfur and polymers [12]. The most effective way for supplying nitrogen to plants consistently and minimizing loss and contamination effects is thought to be coating technology. There are three different types of coated fertilizers: inorganic coating, organic polymer coating, and multifunctional composite coating [17]. When it relates to the effects of use, the physical type of SRF can avoid the limitations that come with rapid fertilizer dilution into the soil; however, it is unable to manage how the dissolved fertilizer behaves in terms of soil transformation [1]. A new category of control release fertilizer is matrix-based fertilizers (MFs). MFs are primarily composed of matrix-based urea and matrix-based compound fertilizer, which are made using similar mechanisms and components. Chemical types of SRFs/CRFs can be divided into two categories: Chemically bonded fertilizers and chemically inhibited fertilizers [1].

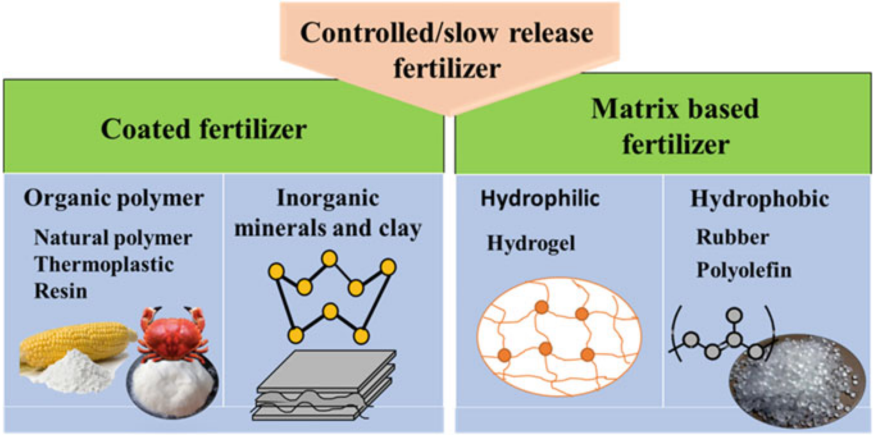


Fig. 1 Classification of controlled-release fertilizer

The effect of this kind of controlled-release fertilizer is better, though the production cost is relatively high. Chemically bonded fertilizers are those that need to be blended with one or more chemical substances through covalent or ionic bonding to create a slightly soluble or insoluble in water. The inclusion of inhibitors allows the chemically inhibited fertilizers to release nitrogen gradually.

3 Clay-Based Hybrid Fertilizers

Clay minerals hydrous layer aluminosilicates constitute with the greater part of the phyllosilicates. Two-dimensional Si–O tetrahedral and Al or Mg-O-OH octahedral arrays are the main constituents of clay minerals [18]. Clay minerals have a special set of attributes, including high cation exchange capacities, capability of act as catalysts capabilities, and plasticity in moist conditions, due to their compact size and high surface area to volume ratio [19]. Clay in nature is hydrophilic. Additionally, clay minerals can have their surface properties changed from hydrophilic to hydrophobic, for instance, making them effective adsorbents and transporters of non-ionic chemical molecules [20]. The maximum number of cations that a particular amount of clay can receive is known as the cation exchange capacity, and this value is constant [21]. It is necessary to alter the clay's surface so that hydrophobic polymers can interact with it. The cation exchange method is typically used to modify clay surfaces [22]. Organoclays, clay nanocomposites, acid- and salt-induced modification of clays, thermally and mechanically induced, and pillared layered clays are just a few examples of modified clays in general. Organoclays are made by substituting organic cations for naturally occurring exchangeable inorganic cations. If interlayer metal cations are switched out for an organic cation such as alkylammonium, the clay surfaces undergo significant modification and develop an organophilic nature. Another method of altering clay is acid treatment, which is mostly employed to enhance the catalytic characteristics of minerals. Since the nature of the clay minerals' surfaces determines their adsorptive and catalytic behavior, an acid treatment will result in the change of original active sites. Thermally and mechanically induced modifications: Thermal modification of the clays can modify their chemical and mineralogical makeup [23].

Hybrid materials are compounds created by the molecular or nanoscale constituents. Typically, one of this constituent is organic in nature, and the other is inorganic. Intercalation clay hybrids exfoliated compounds and sol–gel hybrid materials are frequent varieties of clay hybrid materials. Intercalation compounds are produced when organic compounds are inserted intracrystallinely between the layers of some lamellar materials. Compounds that have been exfoliated or delaminated are produced when clay layers separate, and the resultant platelets are uniformly distributed all across the polymer matrix. The convenience of preparation for the sol–gel technique accounts for its relevance in technology.

The primary starting ingredients for the production of glassware and ceramics as well as the creation of novel organic–inorganic hybrid materials are silicon alkoxides [18].

Clay composites' barrier properties are increased when the clay is modified with polymers, specially surface crosslinking polymers. Fertilizer treated with clay composites also has slow-release properties. Polymer gel comprised surface crosslinking which is more stable than the other polymer and can be attached between the expanding clay's interlayers [24]. Better slow-release properties of modified clay are imparted by these qualities. The surface cross-linked product not only has excellent slow-release properties but also a high capacity for soil moisture preservation, which may greatly improve the efficiency with which fertilizers and water resources are utilized simultaneously. While clay polymer-coated P-fertilizers perform well in calcareous soil, clay polymer-coated N-fertilizers have been proven to be particularly effective in minimizing N losses and enhancing N consumption efficiency in sandy soil [23]. A variety of nanomaterials, including those that are made entirely of the desired nutrient (like hydroxyapatite nanoparticles, which supply P), as well as those that are simply loaded with it, can be used as fertilizers. Currently, it has been demonstrated that nanoclay polymer composites (NCPCs), which are made of sodium alginate, montmorillonite, acrylamide, acrylic acid, and crosslinker, are also effective slow-release substrates for important nutrients including N, P, and K [25] (Table 1).

3.1 Hybrid Nanocomposites

Clay minerals called nanoclays have at minimum one of their measurements in the nanometer range. The fundamental structural component of nanoclays is made up of silicon tetrahedral and aluminum octahedral layers. As previously mentioned, the sheets of montmorillonite, naturally contain negative charges that allow cations to exchange, making them an ideal carrier for a variety of plant nutrients. Nanoclays

Table 1 Examples of clay polymer hybrid composites for sustained-release fertilizer

Clay composite	Fertilizer	Attributes	Reference
Chitosan- montmorillonite clay and paraffin wax	Diammonium phosphates (DAP) fertilizer	Significantly delayed the phosphorus dissolution	[26]
Chitosan-kaolinite	NPK mineral fertilizer	Slow release	[27]
Starch-poly(vinyl alcohol) and bentonite	Diammonium phosphate (DAP)	Reduced the N and P release	[28]
Hydroxyapatite-montmorillonite nanohybrid	Urea	Slow and sustained release of nitrogen	[29]
Poly(acrylicacid-cosodiumacrylate)-montmorillonite	Potassium nitrate	Controlled release	[30]
Acrylic acid, acrylamide halloysite nanotubes	Urea	Controlled urea release	[31]
Sodium alginate and halloysite	Urea	Slow release	[32]
Polyvinyl alcohol montmorillonite	Potassium Phosphate Fertilizer	Controlled release	[33]
Attapulgite clay, ethylcellulose film, and sodium carboxymethylcellulose hydrogel	Urea, ammonium sulfate, and ammonium chloride	Slow release and reduced nutrient loss	[34]
Sodium alginate, acrylic acid, acrylamide, and montmorillonite	NPK mineral fertilizer	Slow-release property and increased the water retention capacity	[35]

have good slow-release qualities, which are consistent with the clay's hydrophobicity and high aspect ratio. This is because numerous studies have employed modified montmorillonite to successfully slow-release a variety of nutrients and fertilizers, such as copper sulfate, urea, and nitrogen fertilizers [36].

Nanofertilizers can supply one or more nutrients to increase growth and productivity. When combined with conventional fertilizer solutions, formulations including nanomaterials boost fertilizer efficacy without the need for additional nutrients [37]. Different methods of nutrient enrichment for fertilizers are possible with the aid of nanotechnology: Coating with a thin protective coating material in nanoscale and encapsulation using nanomaterials. For controlled-release applications in agriculture, nanoclays are one of the most popular nanomaterial employed as a fertilizer carrier. Nanoclays such laponite, hectorite, kaolin, and montmorillonite and hectorite, synthetic montmorillonite, and double-layered hydroxides are examples of synthetic clays used to manufacture composite. Clay particles with at least one dimension smaller than a nanometer are placed in polymer matrix to create nanoclay-polymer composites, a new class of materials with distinct mechanical, rheological, and physical characteristics. Incorporating nanoclay into nanocomposites has benefits for mechanical behavior, solute sorption ability and swelling capacity and increased heat stability [38]. Due to their unique anion exchange capability, nanoclays become superb transporters of nutrients like borate ions, nitrates, and phosphate. The most often used cationic nanoclays as nutrient carriers are kaolinite, montmorillonite, and zeolites [39]. There are two important factors that demonstrate the suitability of nanoclay as a great option to be selected as nutrient transporters or coaters. First, they have the ability to protect nutrient components with the help of physical barriers that are provided by their innate structural elements. Second, by having layers of nanoclays, interactions such as ion exchange or non-electrostatic interactions enable the intercalation of nutrients. With the abovementioned important aspects, nanoclays have the ability to keep nutrients for longer periods of time, increase plant growth rate, improve nitrogen usage efficiency, provide a balanced supply of nutrients, and reduce environmental risks [4]. The methods for assembly rely on the properties of the clay: Layered clays (smectites, vermiculites, and kaolinites) can adsorb various molecules and ions, including polycations, nanoparticles, and polymers, at soft experimental circumstances, producing intercalation compounds and nanostructured materials. Sepiolite and palygorskite, two microfibrous clay minerals, may interact with various organic species through their external surfaces and, in some circumstances, internal surfaces to produce hybrid materials. Clay-derived nanostructured hybrids are becoming more and more sought-after materials due to their structural qualities and practical uses in fields like agriculture and the environment [40].

The use of nanoclay-polymer composites, one of the more recent fertilizer delivery alternatives, may open up new opportunities for managing effective supply of nutrients [41]. There are two types of nanocomposites, intercalated nanocomposites are created when polymer chains penetrate into the clay's interlayer region, forming an organized multiple-layer structure with alternating polymer/inorganic layers spaced repeatedly apart by a few nanometers. The clay layers in the exfoliated nanocomposites delaminate and are scattered randomly throughout the polymer matrix, resulting in broad polymer penetration. The best properties have been reported for exfoliated nanocomposites as a result of the ideal interaction between polymer compound and clay [42]. The degree of phase mixing and the size of each phase's component have a significant impact on the nanocomposite's properties. The nature of the components (polymer matrix, capacity for cation exchange, and nanofiber) as well as the preparation techniques have an impact on the significant differences in the properties of the component that are obtained [24].

3.2 Clay-Coated Fertilizers

Granular fertilizer serves as the base of coated fertilizer, which is then covered with a layer of low water-soluble or water-insoluble inorganic material such as clay or an organic polymer compound using various techniques like heating, drying techniques, spraying, and other methods. This allows the rate at which nutrients diffuse from the core of the membrane to the membrane's exterior to be controlled [43]. The main idea to do so is to coat the fertilizers with such components which are not harmful to the environmental and can provide fertilizers nutrients to plants on need. Inorganic compounds and organic polymers make up the majority of the materials used in coatings. Sulfur coatings, bentonite, and phosphogypsum are examples of inorganic materials, whereas synthetic organic polymers include, polyethylene materials, alkyd resin and polyurethane, etc. [44]. There are many types of coating, among them the coating of fertilizers with clay polymers is the most efficient because it has more efficiency than other coating subjects [45]. There are several ways to incorporate clay into fertilizer-coating polymers to make them incredibly absorbent then they can store water for a very long time and release it to plants as needed. When there are layered materials present, the monomer species undergo in situ polymerization. The solution with monomer first causes the polymer clays to swell before it begins to polymerize between intercalated sheets. When necessary, polymerization can be initiated by heat, radiation, the diffusion of a suitable initiator, an organic initiator, or a catalyst fixed through cation exchange inside the interlayer before the inflammation stage. This procedure involves mixing silicate layers with a polymer matrix while it is still molten. In case that, the layers of the surface are well matched to the selected polymer, and the polymer can seep into the interlayer gap and form an exfoliated or intercalated nanocomposite. Usually, clay is combined with molten polymer during extrusion so that the polymer's chains can intercalate between the surfaces of the clay layers [46]. To boost the needed characteristics of clay polymers, supercritical fluids have been used in their synthesis. Compared to other approaches, this one has a lot of benefits. Montmorillonite is regarded as a swelling mineral because it has alkali metal ions trapped between silicate sheets. As a result, polar solvents including supercritical CO_2 and water like solvents can swell this [47]. A two-step process called sol–gel involves the first stage, sol, and the second, gel. Gel is the connected framework that developed between the phases, whereas sol is the suspension of solid particle. By applying hydrothermal treatment of the gel, including the polymers, silicate clays are directly crystallized using this process. This is a simple process, lower processing temperature and higher chemical homogeneity. The main advantage of the sol–gel process is its compatibility with the polymers and the polymerization processes, and this allows the formation of nanoparticles in the presence of organic molecules. This method produced high purity product such as polymers of clay.

3.3 Controlled-Release Mechanism of Clay-Coated Fertilizer

To regulate the delivery of nutrients into the soil and to match plant demand, controlled-release fertilizer provides an effective tool. They may offer high-use efficiency and minimize the environmental impact. The multistage diffusion model states that water permeates the covering and condenses on the solid fertilizer core before partially dissolving. Granules will enlarge and an osmotic pressure will form, causing one of the two processes. This osmotic pressure can lead to a coating rupture and the entire fertilizer core being discharged spontaneously in one procedure. Failure mechanism or catastrophic release is the term used to describe this process. In the second procedure, the membrane withstands the increasing pressure and the core fertilizer is released gradually via diffusion: This is known as the "diffusion mechanism." Failure mechanism or catastrophic release is the term used to describe this process. The conventional method for releasing coated fertilizer involves the release of nutrients from the soil's polymer-fertilizer interface, which is triggered by water. The factors controlling the release mechanism are diffusion or swelling, deterioration of the polymer covering, and dissolution [48]. Nutrients can be released at the delivery system as a result of polymer degradation, which can happen either overall or at the surface. The hydrolytic or enzymatic response of the microorganisms at the surface of the coated granules causes erosion at the surface. However, in the case of bulk erosion, hydrolytic activities cause polymer degradation after water uptake [49].

Chemical fertilizers' release curve is distinguished by an excessively strong initial release known as the "burst" and an excessively slow release of the last quarter to third of the nitrogen known as the "tailing effect," which is very different from the pattern of nutrient uptake by plants [13]. Fertilizers with hydrophobic coatings, particularly clay polymer-coated fertilizers, offer effective release control. The general pattern of nutrient release and plant absorption from coated fertilizers is temporal release with or without burst, which may follow the pattern of parabolic release through the pattern of linear release to sigmoidal release [50]. Lag phase, steady release, and degrading phase are the three stages for the release of nutrients from controlled-release fertilizer (Fig. 2). In the first stage of the control release mechanism, soil moisture wets the coating's cracks and seeps into the core. Here, a small portion of the fertilizer is dissolved. At this particular point, the driving force is the vapor pressure gradient, and fertilizer is not released. As an alternative, CRFs made of hydrogel will expand when exposed to water and absorb it. The time it takes to fill the internal spaces with the necessary amount of water or to maintain a steady state between the fluxes of water and solute entering and exiting, respectively, could be the reason of the lag that is present at this stage. The fertilizer is gradually released through the pores in the polymer coating or the swollen hydrogel network in the subsequent phase as more water percolates into the core and more solid fertilizer dissolves, increasing osmotic pressure and accumulating the necessary water volume of saturated solution. Because the concentration of the solution inside the granule remains saturated, the diffusion to the soil is ongoing. The covering material collapses when the pressure

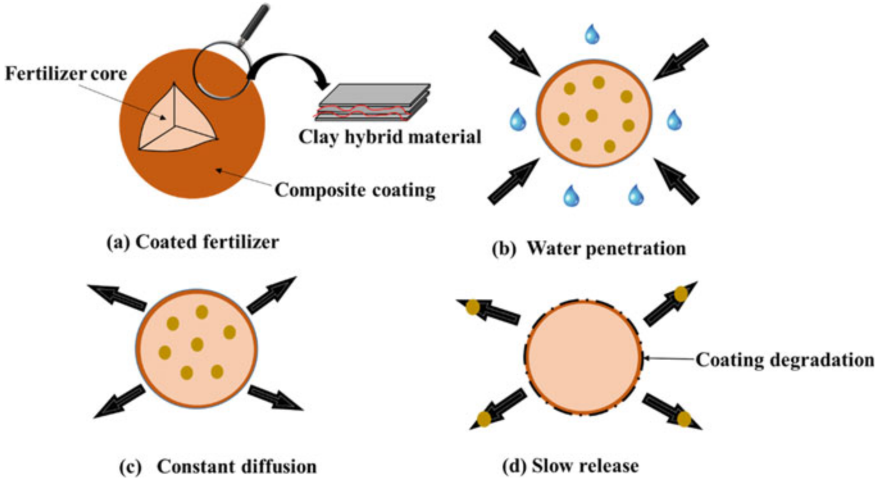


Fig. 2 Controlled-release mechanism of clay hybrid fertilizer

rises over a predetermined threshold, allowing the fertilizer inside to immediately burst out. The concentration gradient, driving force, and consequently the release rate have all decreased because the majority of the fertilizer has been dissolved and released during the degrading phase [51]. An alternative way to represent it is with a sigmoidal (S-shaped) nutrition release profile. This suggests that the release process is complicated and nonlinear. Since it exhibits controlled-release characteristics that satisfy crop nutritional needs, scientists would prefer to achieve a sigmoidal release profile with their formulations of clay hybrid controlled-release formulations [44].

4 Challenges and Future Aspects

Clay hybrid materials-based controlled-release formulation reduce nutrient leaching improve the efficiency of fertilizer and minimize the hazards to environment as compared to conventional fertilizers since they release nutrients more gradually. The controlled-release fertilizer formulation's efficiency, dependability, and cost-effectiveness reduce food crises and other difficulties with crop output. At crucial times for crop growth, it reduces the need for human labor and lessens stress and toxicity. The critical variables that affect how quickly nutrients are released from granules are fumigation of soil, amount of moisture and temperature. Several nanoclays are not readily available in adequate amounts despite the fact that clay minerals are common in nature; thus, their synthesis will be highlighted in the field of clay research and could result in a breakthrough in the study of nanocomposites. It would be ideal to have more information on occupational exposure to nanoclays during production, development, and their application. For many years, scientists prepared clay polymers using three main techniques: In situ polymerization, intercalation, and template synthesis. These conventional techniques have advantages as well as drawbacks. New techniques including supercritical CO_2 and use of sol–gel technology also available now. The constraints of these approaches must be addressed, and more adjustments should be made to enhance the production techniques. One of them is the employment of these methods on a large scale to increase plant yield by supplying nutrients when they are needed. The majority of research to date has been conducted in this area in laboratory settings or through pot experiments. Researchers and scientists have been working to modify and improve in the near future would be used on large scale. Consequently, to create N- and P-fertilizers with high usage efficiency, future inventions should be conducted in the field utilizing various clays and clay composites.

Acknowledgement Financial assistance by RG/2021/AG/02 grant received from the National Science Foundation, Sri Lanka.

References

1. Al-Rawajfeh, A.E., Alrbaihat, M.R., AlShamaileh, E.M.: Characteristics and types of slow- and controlled-release fertilizers. In: Controlled Release Fertilizers for Sustainable Agriculture, pp. 57–78. Elsevier (2021)
2. Marcińczyk, M., Oleszczuk, P.: Biochar and engineered biochar as slow-and controlled-release fertilizers. J. Clean. Production. **130685** (2022)
3. Chen, J., Lü, S., Zhang, Z., Zhao, X., Li, X., Ning, P., Liu, M.: Environmentally friendly fertilizers: A review of materials used and their effects on the environment. Sci. Total Environ. **613**, 829–839 (2018)
4. Vejan, P., Khadiran, T., Abdullah, R., Ahmad, N.: Controlled release fertilizer: A review on developments, applications and potential in agriculture. JCR **339**, 321–334 (2021)
5. Iqbal, A., He, L., Khan, A., Wei, S., Akhtar, K., Ali, I., Ullah, S., Munsif, F., Zhao, Q., Jiang, L.: Organic manure coupled with inorganic fertilizer: An approach for the sustainable production of rice by improving soil properties and nitrogen use efficiency. Agron. **9**(10), 651 (2019)
6. Rajan, M., Shahena, S., Chandran, V., Mathew, L.: Controlled release of fertilizers—concept, reality, and mechanism. In: Controlled Release Fertilizers for Sustainable Agriculture, pp. 41–56. Elsevier (2021)
7. Xiang, L., Liu, S., Ye, S., Yang, H., Song, B., Qin, F., Shen, M., Tan, C., Zeng, G., Tan, X.: Potential hazards of biochar: The negative environmental impacts of biochar applications. J. Hazard. Mater. **420**, 126611 (2021)
8. Rayne, N., Aula, L.: Livestock manure and the impacts on soil health: A review. Soil Systems **4**(4), 64 (2020)
9. Dróżdż, D., Wystalska, K., Malińska, K., Grosser, A., Grobelak, A., Kacprzak, M.: Management of poultry manure in Poland–Current state and future perspectives. J. Environ. Manage. **264**, 110327 (2020)
10. Kumar, R., Kumar, R., Prakash, O.: Chapter-5 the Impact of Chemical Fertilizers on Our Environment and Ecosystem. Chief Ed. **35**, 69 (2019)
11. Reynolds, T.W., Waddington, S.R., Anderson, C.L., Chew, A., True, Z., Cullen, A.: Environmental impacts and constraints associated with the production of major food crops in Sub-Saharan Africa and South Asia. Food Secur. **7**(4), 795–822 (2015)

12. Subbarao, C.V., Kartheek, G., Sirisha, D.: Slow release of potash fertilizer through polymer coating. Int. J. Appl. Sci. Eng. **11**(1), 25–30 (2013)
13. Shaviv, A.: Advances in controlled-release fertilizers. Adv. Agron. **71**, 1–49 (2001)
14. Azeem, B., KuShaari, K., Man, Z.B., Basit, A., Thanh, T.H.: Review on materials & methods to produce controlled release coated urea fertilizer. JCR **181**, 11–21 (2014)
15. Du, C.-w., Zhou, J.-m., Shaviv, A.: Release characteristics of nutrients from polymer-coated compound controlled release fertilizers. J. Polym. Environ. **14**(3), 223–230 (2006)
16. Wang, Y., Liu, M., Ni, B., Xie, L.: κ-Carrageenan–sodium alginate beads and superabsorbent coated nitrogen fertilizer with slow-release, water-retention, and anticompaction properties. Ind. Eng. Chem. Res. **51**(3), 1413–1422 (2012)
17. Ni, B., Liu, M., Lü, S., Xie, L., Wang, Y.: Multifunctional slow-release organic−inorganic compound fertilizer. J. Agric. Food Chem. **58**(23), 12373–12378 (2010)
18. Choudhury, T., Do Nascimento, G.M.: Clay hybrid materials. Appl. Clay Sci. 17–32 (2020)
19. Moraes, J.D.D., Bertolino, S.R.A., Cuffini, S.L., Ducart, D.F., Bretzke, P.E., Leonardi, G.R.: Clay minerals: Properties and applications to dermocosmetic products and perspectives of natural raw materials for therapeutic purposes—A review. Int. J. Pharm. **534**(1–2), 213–219 (2017)
20. Yuan, G.D., Theng, B.K.G., Churchman, G.J., Gates, W.P. Clays and clay minerals for pollution control. In: Developments in Clay Science, vol. 5, pp. 587–644. Elsevier (2013)
21. Kumari, N. and Mohan, C.: Basics of clay minerals and their characteristic properties. Clay Clay Miner. **24**, 1–29 (2021)
22. Singla, P., Mehta, R., Upadhyay, S.N.: Clay modification by the use of organic cations. Green Sustain. Chem. **2**(1), 21–25 (2012)
23. Basak, B.B., Pal, S., Datta, S.C.: Use of modified clays for retention and supply of water and nutrients. Curr. Sci. **102**(9), 1272–1278 (2012)
24. Kotal, M., Bhowmick, A.K.: Polymer nanocomposites from modified clays: Recent advances and challenges. Prog. Polym. Sci. **51**, 127–187 (2015)
25. Okey-Onyesolu, C.F., Hassanisaadi, M., Bilal, M., Barani, M., Rahdar, A., Iqbal, J., Kyzas, G.Z.: Nanomaterials as nanofertilizers and nanopesticides: An overview. Chem. Select **6**(33), 8645–8663 (2021)
26. El Assimi, T., Lakbita, O., El Meziane, A., Khouloud, M., Dahchour, A., Beniazza, R., Boulif, R., Raihane, M., Lahcini, M.: Sustainable coating material based on chitosan-clay composite and paraffin wax for slow-release DAP fertilizer. Int. J. Biol. Macromol. **161**, 492–502 (2020)
27. Eddarai, E.M., El Mouzahim, M., Boussen, R., Bellaouchou, A., Guenbour, A., Zarrouk, A.: Chitosan-kaolinite clay composite as durable coating material for slow release NPK fertilizer. Int. J. Biol. Macromol. **195**, 424–432 (2022)
28. Sarkar, A., Biswas, D.R., Datta, S.C., Dwivedi, B.S., Bhattacharyya, R., Kumar, R., Bandyopadhyay, K.K., Saha, M., Chawla, G., Saha, J.K.: Preparation of novel biodegradable starch/ poly (vinyl alcohol)/bentonite grafted polymeric films for fertilizer encapsulation. Carbohydr. Polym. **259**, 117679 (2021)
29. Madusanka, N., Sandaruwan, C., Kottegoda, N., Sirisena, D., Munaweera, I., De Alwis, A., Karunaratne, V., Amaratunga, G.A.J.: Urea–hydroxyapatite-montmorillonite nanohybrid composites as slow release nitrogen compositions. Appl. Clay Sci. **150**, 303–308 (2017)
30. Ganguly, S., Das, N.C.: Water uptake kinetics and control release of agrochemical fertilizers from nanoclay-assisted semi-interpenetrating sodium acrylate-based hydrogel. Polym. Plast. Technol. Eng. **56**(7), 744–761 (2017)
31. Wei, H., Wang, H., Chu, H., Li, J.: Preparation and characterization of slow-release and water-retention fertilizer based on starch and halloysite. Int. J. Biol. Macromol. **133**, 1210–1218 (2019)
32. Shen, Y., Wang, H., Li, W., Liu, Z., Liu, Y., Wei, H., Li, J.: Synthesis and characterization of double-network hydrogels based on sodium alginate and halloysite for slow release fertilizers. Int. J. Chem. Biochem. Sci. **164**, 557–565 (2020)
33. Hakim, S., Darounkola, M.R.R., Barghemadi, M., Parvazinia, M.: Fabrication of PVA/nanoclay hydrogel nanocomposites and their microstructural effect on the release behavior of a potassium phosphate fertilizer. J. Polym. Environ. **27**(12), 2925–2932 (2019)

34. Ni, B1., Liu, M., Lu, S., Xie, L., Wang, Y.: Environmentally friendly slow-release nitrogen fertilizer. J. Agric. Food Chem. **59**(18), 10169–10175 (2011)
35. Rashidzadeh, A. and Olad, A.: Slow-released NPK fertilizer encapsulated by NaAlg-g-poly (AA-co-AAm)/MMT superabsorbent nanocomposite. Carbohydr. Polym. **114**, 269–278 (2014)
36. Merino, D., Tomadoni, B., Salcedo, M.F., Mansilla, A.Y., Casalongué, C.A., Alvarez, V.A.: Nanoclay as carriers of bioactive molecules applied to agriculture. Handb. Nanomater. Nanocomposites Energy Environ. Appl. 1–22 (2020)
37. Kalia, A., Sharma, S.P., Kaur, H., Kaur, H. Novel nanocomposite-based controlled-release fertilizer and pesticide formulations: Prospects and challenges. In: Multifunctional Hybrid Nanomaterials For Sustainable Agri-Food And Ecosystems, pp. 99–134. Elsevier (2020)
38. Zhang, J., Wang, A.: Study on superabsorbent composites. IX: synthesis, characterization and swelling behaviors of polyacrylamide/clay composites based on various clays. React. Funct. Polym. **67**(8), 737–745 (2007)
39. Benício, L.P.F., Constantino, V.R.L., Pinto, F.G., Vergütz, L., Tronto, J., da Costa, L.M.: Layered double hydroxides: new technology in phosphate fertilizers based on nanostructured materials. ACS Sustain. Chem. Eng. **5**(1), 399–409 (2017)
40. Vejan, P., Khadiran, T., Abdullah, R., Ahmad, N.: Controlled release fertilizer: A review on developments, applications and potential in agriculture. J. Control. Release **339**, 321–334 (2021)
41. Verma, Y., Datta, S.C., Mandal, I.K., Sarkar, D.: Effect of phosphorus loaded organically modified nanoclay-polymer composite on release and fixation of phosphorus and its uptake by wheat (Triticum aestivum L.). J. Pure. Appl. Microbiol. **10**(3), 2299–2306 (2016)
42. Mukhopadhyay, R., De, N.: Nano clay polymer composite: synthesis, characterization, properties and application in rainfed agriculture. Global J. Bio. Biotechnol. **3**(2), 133–138 (2014)
43. Yuan, S., Cheng, L., Tan, Z.: Characteristics and preparation of oil-coated fertilizers: A review. JCR **345**, 675–684 (2022)
44. Lawrencia, D., Wong, S.K., Low, D.Y.S., Goh, B.H., Goh, J.K., Ruktanonchai, U.R., Soottitantawat, A., Lee, L.H., Tang, S.Y.: Controlled release fertilizers: A review on coating materials and mechanism of release. Plants. **10**(2), 238 (2021)
45. Zhang, S., Fu, X., Tong, Z., Liu, G., Meng, S., Yang, Y., Helal, M.I.D., Li, Y.C.: Lignin–clay nanohybrid biocomposite-based double-layer coating materials for controllable-release fertilizer. ACS Sustain. Chem. Eng. **8**(51), 18957–18965 (2020)
46. Nguyen, Q.T., Baird, D.G.: Preparation of polymer–clay nanocomposites and their properties. Adv. Polym. Technol. **25**(4), 270–285 (2006)
47. Nisar, S., Shehzad, M.R., Rafiq, M., Kousar, S., Abdul, H.: Production of clay polymers for fertilizer coating. Int. J. Chem. Biochem. Sci. **12**, 122–129 (2017)
48. Lu, S.M., Chang, S.-L., Ku, W.-Y., Chang, H.-C., Wang, J.-Y., Lee, D.-J.: Urea release rate from a scoop of coated pure urea beads: Unified extreme analysis. Chin. J. Chem. Eng. **38**(3–4), 295–302 (2007)
49. Guo, M., Liu, M., Zhan, F., Wu, L.: Preparation and properties of a slow-release membrane-encapsulated urea fertilizer with superabsorbent and moisture preservation. Ind. Eng. Chem. Res. **44**(12), 4206–4211 (2005)
50. Ganetri, I., Essamlali, Y., Amadine, O., Danoun, K., Aboulhrouz, S., Zahouily, M. Controlling factors of slow or controlled-release fertilizers. In: Controlled Release Fertilizers for Sustainable Agriculture, pp. 111–129. Elsevier (2021)
51. Shaviv, A., Raban, S., Zaidel, E.: Modeling controlled nutrient release from polymer coated fertilizers: Diffusion release from single granules. Environ. Sci. Technol. **37**(10), 2251–2256 (2003)

Nanoclay Composites as Agrochemical Carriers

Maheshika Perera, L. Jayarathna, D. M. D. Yakandawala, and S. Seneweera

Abstract Agricultural production systems are facing major challenges as a result of rapid urbanization and extreme climate events. There are various accessible gears in current science to circumvent these limitations. Advanced nanotechnology can be used for achieving food security while improving soil fertility, crop productivity, and maintaining the sustainability of our agriculture system. The use of nanocarriers in agriculture sector such as nanofertilizers, nanopesticides, and nanoherbicides is instrumental for improvement in crop productivity. However, there is a significant opportunity to use nanomaterials in agriculture to increase crop performance. In addition, nanocarrier materials, which have been precisely engineered, play a major role in facilitating targeted delivery. There are numerous nanocarriers used in agriculture such as metal nanoparticles, carbon nanotubes, graphene and graphene oxides, polymers, nanoclays, lipids, and. Among those nanocarriers nanoclay plays a very specific role in agrochemical delivery. The fundamental rationale for such specialized delivery qualities is due to the unique properties of the materials, such as low cost, nontoxicity, natural abundance, correct compatibility, and intermolecular forces, which in long-term help to develop continuous release of inactive ingredient. Overall, this chapter will discuss the underlying process of nanomaterials-based active ingredient release mechanisms related to a variety of plant applications.

Keywords Nanoclay · Nanofertilizers · Nanoherbicides · Nanopesticides · Agriculture

---

M. Perera (✉) · L. Jayarathna
National Institute of Fundamental Studies, Kandy, Sri Lanka
e-mail: maheshikapavithra@gmail.com

D. M. D. Yakandawala
Department of Botany, University of Peradeniya, Peradeniya, Sri Lanka

S. Seneweera
University of Melbourne, Melbourne, Australia

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5_26

1 Introduction

Extensive research has been conducted on a global scale to implement nanotechnology in agriculture to increase crop yield. Despite all efforts, Food Security, required by Food and Agricultural Organization of the United Nations (FAO) has not yet been realized [10]. On the other hand, limited land is available for cultivation, while the population is expected to reach 9–10 billion by 2050. Thus, global food requirements have also risen, and the anticipated per capita food requirement is likely to double by 2050 [51]. It is needed to increase agricultural productivity and industry sustainability. Other hand, resource-constrained environmental issues that the agricultural sector faces include climate change, urbanization brought on by changes in lifestyles, and excessive use of resources like high-quality rock phosphate, natural gas, and petroleum which all have an impact on crop productivity. These issues will significantly impact developing nations where agriculture forms the foundation of their national economies. Consequently, most of the countries including developing countries invest a formidable amount of funds in nanotechnology research in the agriculture sector aiming to large benefit from these technology [58].

Many nanomaterials have been developed for agricultural applications, including nanofertilizers, nanoherbicides, and nanopesticides, designed to reduce their current usage of them. These materials contributed to an increase in food production and quality as well as industry sustainability [67]. Immobilization, encapsulation, and vehiculation are the main technology that have been widely used in used in preparing nanomaterials. Thus, loading an active ingredient into the available space of a nanometric material can be referred to as nanovehiculization.

The normal size of these agents usually ranges from 100 to 500 nm with a limit of 1000 nm [21]. These incorporated active ingredients can be adsorbed inside the nanovehicle in liquid, solid, or molecular dispersive forms. There are different types of nanovehicles are used in the delivery of agrochemical agents including clays, polymers, and liposomes. Among them, clays are heavily used, simply because of inexpensive naturally occurring minerals with variability in chemical constitution [22].

Nanoclay originates from naturally occurring clays, which are mainly made up of finely divided mineral particles. The major portion of clay minerals is covered by layered silicates, which are made up of silicon and oxygen bonds with some other elements. They can be thought of as a “stack” of two-dimensional single, double, or multilayers, which are formed by corner-linked silicate tetrahedrons. Due to the absence of chemical bond between layers of the clay geometry, the capacity of stacks layers increases leading to better absorption and dissipation of water and other available molecules [3, 44]. The properties of nanoclay demonstrate as an excellent carrier for agrochemical applications. These properties can also be altered chemically, allowing these materials to be used in a variety of agricultural applications while also promoting environmentally friendly and economically viable agronomic practices.

2 Nanoclay Mineral

Nanoclays have a distinct structure and are used as commercial minerals in various industries. One of the most essential characteristics of nanoclay is its high capacity to load agrochemicals while lowering production costs and protecting the environment. Further, nanoclays are abundant in nature and are represented in the major group of clay minerals. The term “clay mineral” refers to phyllosilicate minerals and to minerals that impart plasticity to clay and which harden upon drying or firing. Clay minerals are layer silicates that are formed as a result of chemical weathering of other silicate minerals [1]. In clay minerals, sheet-like structures are called sheet-structure silicates and phyllosilicates. The silicates’ geometry is laid out like pages of a book, and the interlayers are held together by Van der Waals forces. Phyllosilicates are classified as aluminosilicates in the silicate group; they are made up of sheets of aluminium and silicon oxides stacked on top of each other [28]. They are the basic unit structure of nanoclays and combined to make four layers of silicon tetrahedra, $[SiO_4]^{4-}$, and/or aluminium octahedral, $[AlO_3(OH)_3]^{6-}$.

Furthermore, based on the number of sheets and how these layers are stagnated, there can be three distinct groups, including 1:1, 2:1, and 2:1:1 phyllosilicate (Fig. 1). Understanding the physical and chemical properties of these composites is crucial, as is the loading capacity of the chemicals that can be incorporated into nanoclay. Understanding the physical and chemical properties of these composites is crucial, as their loading capacity is highly dependent on nanoclays’ physical–chemical nature [1].

3 Nanoclay Type

Type 1:1 phyllosilicate consists of sheets self-possessed with tetrahedral and an octahedral layer. Minerals like kaolinite, halloysite, dickite, nacrite, etc., fall under this category. The use of these nanoclays for the vehiculation of active substances is limited because kaolinite does not have the ability to separate its sheets and the halloysite has a hollow tubular shape. Type 2:1 phyllosilicate has two tetrahedral layers separated with an octahedral layer. This is the most common type of nanoclay used as a vehicle to transport substances, and it includes clay minerals like montmorillonite, vermiculite, pyrophyllite, mica, smectite, and others. In the type of 2:1:1 has an octahedral layer adjacent to another octahedral layer arranged between two tetrahedral layers [41]. But this type of clay also not under the category of expanding, therefore, the usage as a vehiculization are not common [44].

The three types of phyllosilicates have distinct properties that influence swelling, expandability, and non-expandability. However, most of the natural nano-clays belong to the smectite group including montmorillonite (MMT), hectorite, saponite, laponite, etc. [46]. Montmorillonite (MMT) has greater abundance and higher aspect ratio (length/thickness ratio of its sheets) which allows a higher nutrient loading capability [6] suggesting to use in many applications. The tetrahedral layers are formed by

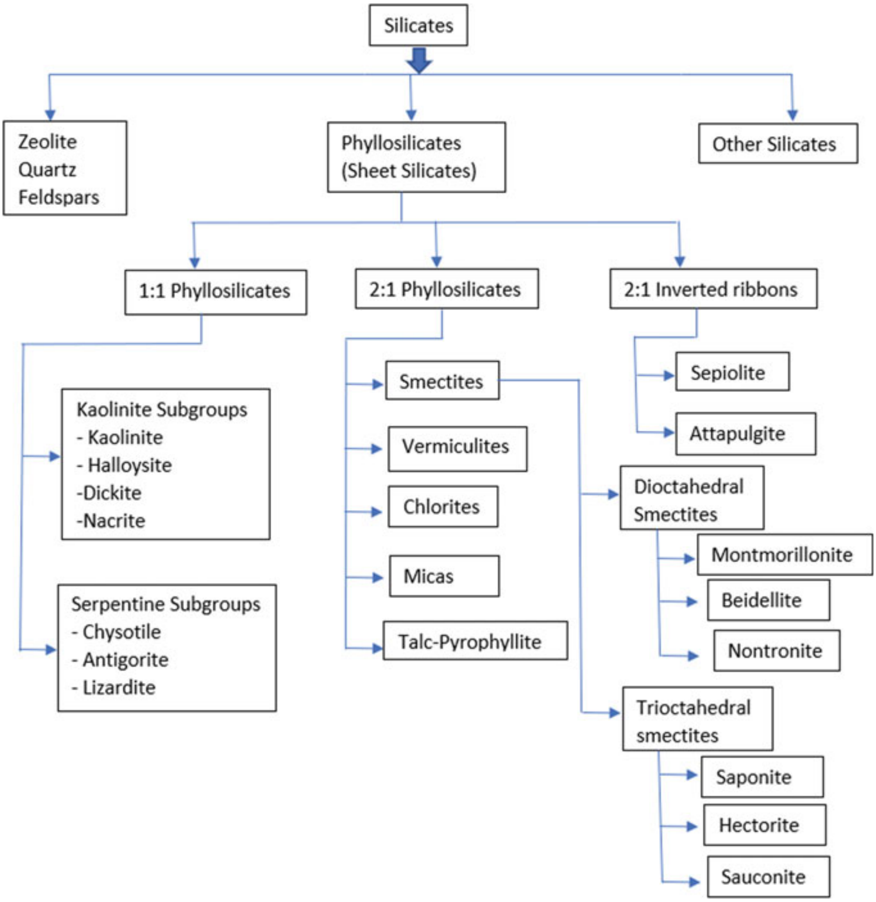


Fig. 1 Classification of silicates and clay minerals [66]

silicon atoms coordinated by four oxygen atoms. Three of these oxygens are shared by neighbouring tetrahedra, thus forming a tetrahedral layer of hexagonal geometry [21].

Further, clays can be modified using both physical structure and chemical composition. The type of interaction, however, is determined by the chemical nature of the substance to be hosted [3, 15]. There are various types of bonding involved in this modification, including hydrogen bonding, ion–dipole, covalent bonding, ionic pairs, ion-pi interactions, dipole–dipole interactions, and cation exchange, which is the most prevalent [61].

However, positively charged elements can be easily replaced in MMT layers through a cation exchange mechanism. For example, it is possible to remove organic cations with inorganic cations which electrostatically interact with clay sheets [4]. In addition, the porosity of clay minerals can be increased via acidic treatments. Nonionic substances can be incorporated to the nanoclays through the interaction between the interlaminar inorganic ions and the polar groups of nonionic molecules [38]. These attributes offer excellent opportunities for chemical modification and improve the chemical loading efficiency.

The structure and composition of clay minerals determine their physical and chemical properties. Important physical and chemical characteristics of clay materials are particle size, shape, and distribution. Mineralogy surface area, charge, and chemistry pH Ion exchange capacity brightness and colour, sorption capacity, rheology, ceramic properties, and dispensability. The physical and chemical characteristics of kaolinite, mica, and smectite (bentonite) are discussed in the following sections.

3.1 Kaolinite

The chemical formula of the clay mineral kaolinite is $Al_2SiO_5(OH)_4$. This is a primary user's mineral. It is a layered silicate mineral composed of one tetrahedral sheet of silica (SiO_4) linked to one octahedral sheet of alumina (AlO_6) octahedra via oxygen atoms. Kaolinite is the main component of kaolin. This mineral is formed due to the process of rock weathering. It is either white or slightly coloured. Kaolinite is made up of tiny, thin, pseudohexagonal, flexible sheets of triclinic crystal which have a diameter of 0.2–12 μm. The density of the material is 2.1–2.6 g/cm^3. The cation exchange capacity of kaolinite ranges between 2 and 10 meq/100 g, which is significantly lower than that of montmorillonite. Tetrahedral layers of silicon and octahedral layers of aluminium make up the sheets, which are neutrally charged. The distance from the surface of a sheet to the other (reticular equidistance) is equal to 0.7 nm [12] demonstrating large physical plasticity to accommodate or absorb materials of interest.

Kaolin clay has many industrial applications such as it is used as a filler in the paper and plastic industries as a coating because of its unique size and shapes [28]. In the production of ceramic raw materials, a chemically inert structure and fine particle size with a white hue produce high-quality materials. Kaolinite is also mainly used as a catalyst as well as an adhesive agent, and use an adsorbent for water treatment. The major portion of kaolinite can be covered SiO_2, Al_2O_3, H_2O and a minor portion is Mg, K, Fe, Ti, etc., elements [37]. In contrast to other clay materials, kaolinite makes it simple to remove the elements that it has adsorbed. This is due to the fact that the molecules that are adsorbed form bonds between the layers of kaolinite, which makes them simple to release. Upon heating, kaolinite starts to lose water at approximately 400 °C, and the dehydration approaches completeness at approximately 525 °C. The dehydration depends on the particle size and crystallinity of the materials [11, 57].

3.2 Smectite

Smectite is a mineral mixture of various swelling sheet silicates (phyllosilicates), which are clay minerals with a three-layer 2:1 structure. It is predominantly composed of montmorillonite, but secondary minerals such as quartz and calcite are frequently present. Due to its distinctive properties, smectite nanoclay is largely unexplored in the field of nanocomposites. For instance, the colours of fresh bentonites range from white to pale green or blue, but after exposure, they become yellow, red, or brown. The primary characteristics of smectite are its ability to absorb large quantities of water and its capacity to increase its volume by 12–15 times its dry mass, and it has high cation exchange capacity. In most instances, exchanges of silicon by cations lead to an excess of negative charges in the lattice, which is then balanced by cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) in the interlayer space [27, 62]. It may be possible for these cations to intercalate due to their lower binding energy.

Montmorillonite (MMT), one of these smectite nanoclays, has a high cation exchange capacity (about 100 meq/100 g). The cation capacity is also influenced by particle size [14]. Clay minerals have the ability to organophilically bind organic cations, surfactants, proteins, dyes, and so on because of their cation exchange capacity [8]. Inorganic cations are also incorporated via the intercalation [52]. Apart from this physical characteristic of bentonite is explained whether the montmorillonite has uniform thickness of water layers or it has a mixture of hydrates with water layers. At the same time loss of absorbed water between the silicate sheets happens normally at low temperatures at around 100–200 °C. Also, structural water loss starts at 450–500 °C and is completed at 600–750 °C. Although, heating to 800–900 °C breaks the crystal lattice and synthesis a range of phases, including mullite, cristobalite, and cordierite [53]. To enhance the utilization and commercial value of bentonite, the ability of taking up water affects [16].

3.3 Mica

Micas are a class of silicate minerals distinguished by the ability of individual mica crystals to be easily split into extremely thin elastic plates. This feature is known as perfect basal cleavage. Mica group clay minerals are also clay minerals with a 2:1 ratio that is similar to the type of clay minerals [54]. This group of clay minerals is also known as illite. The common mica group minerals include muscovite, phlogopite, and biotite. The chemical formula for mica is $Si_8\ (Al, Mg, Fe)_4\ (OH)_4 \cdot (KH_2O)_2$. In mica clay minerals, isomorphic substitution occurs in the tetrahedral layer, most commonly by replacing Si^{4+} with Al^{3+}. It has been demonstrated that charge imbalance influences the incorporation of K^+ ion into the interlayer [26]. This ion imbalance is the result of the tetrahedral layers, and as a consequence, the K^+ ion is strongly bound in the interlayer as well, making it impossible for it to be exchanged. The potassium atom can exactly fit into the hexagonal hole in the tetrahedral sheet and form a strong interlayer bonding [39]. The common mica group minerals include muscovite, phlogopite, and biotite. Most of the natural illites are actually mixed layers of muscovite-like minerals and smectite-like minerals. Illites make up the bulk of ancient shales, and illitization reactions are common during late diagenesis of siliciclastic materials [32, 17].

4 Fertilizers Used in Agriculture Ecosystems

A material of natural or synthetic origin that is applied to soil or to plant with the intention of supplying plant nutrients is referred to as a fertilizer. There is a wide variety of fertilizer available, derived from both natural and synthetic sources. Fertilization in most modern agricultural practises focuses on the three main macronutrients of nitrogen (N), phosphorus (P), and potassium (K), with the occasional addition of micronutrients. Plants are taken up these macronutrients as N, P_2O_5, and K_2O, respectively [13].

Further, intensive cropping led to the removal of a significant quantity of these nutrients from the soil; it is necessary to supplement those nutrients in order to release the full potential of the soil's yield. These nutrients could be classified into two major categories as macronutrients and micronutrients [21]. Fertilizers can be applied by farmers in a number of different ways, including dry application, pelletized application, or liquid application. N.P.K. solid fertilizers cab found in the market in different commercial names including urea, ammonium, potassium, calcium nitrates, mono- and di-ammonium phosphate, and potassium chloride, and sulphate. N.P.K. fertilizers can also be found as liquid fertilizers such as urea ammonium nitrate and ammonium polyphosphate [55].

The nutrient requirements of plants vary depending on their developmental stage. For example, early growth necessitates more N, whereas tillering and stem elongation necessitate more P and K. Plants should be supplied with at least critical nutrient requirements for optimum growth; if any of the nutrients are deficient, the deficient nutrient will act as a limiting factor for plant growth. In order to increase yield and plant resistance to abiotic and biotic stresses, it is essential to maintain critical nutrient requirements constant for all nutrients. The capacity of crops to absorb and utilize nutrients for maximum yields is known as nutrient use efficiency (NN.U.E. The uptake, assimilation, and utilization of nutrients are thus the three main processes that the NN.U.E. concept entails in plants. Poor NN.U.E. is one of the main factors in fertilizer use in agriculture. The maximum nutrient use efficiency in our agricultural systems is around by 40%, but this depends on a variety of factors, including plant type, environment, and fertilizer type. Therefore, crops are currently supplied with a massive amount of fertilizer worldwide [60].

The excessive use of these chemical fertilizers has many negative effects on the environment, including water eutrophication, soil degradation, and an increase in nitrous oxide levels that contribute to global warming and also an additional cost of production. For example, N, P, and K applied to the soil are lost between 50 and 70% due to surface runoff, leaching of nitrates, and volatilization, which contributes to global warming [2]. Therefore, fertilizer use efficiency should be increased, which will have multiple positive effects on the economy and the environment [25]. These goals can only be achieved by understanding plant nutrient uptake kinetics and developing fertilizers with the chemistry to synchronize supply and demand.

5 Nanoclays as Vehicles

5.1 Nanofertilizer

The amount of land that can be used for farming is decreasing every day because of erosion, pollution, and urbanization. On the other hand, agricultural production needs to increase to meet growing population demand for food security. In recent years, nanofertilizers have been made, which need to make fertilizer use much more efficient. But the process of making nanofertilizer is expensive, and the way it works could also be improved. This technology is likely to be a big part of the future of agriculture all over the world. Mainly, there are two types of fertilizers are used in agriculture including slow release and control release fertilizers [35]. The benefits of controlled-release fertilizers include a lower rate of loss, a steady supply of nutrients, lower application rates, and, as a result, less damage to the environment. They support in meeting the nutritional requirements of the plant with a single dose or application, just like slow-release fertilizers, by making the nutrient only available when required. Additionally, this reduces denitrification losses, nutrient leaching, and volatilization [19]. There are many different types of nanomaterials that can be used as carriers, such as nanoclay, hydroxyapatite nanoparticles, mesoporous silica, carbon-based nanomaterials, polymeric nanomaterials, and nanocomposites [45, 59]. Nano-clays are one of these nanomaterials, and they stand out from other materials due to their high surface area, ionic charge, and usefulness in retaining plant nutrients. They also play a crucial role in soil pH buffering. Another advantage of using nanoclay is that it is inexpensive and environmentally friendly [45].

Typically, smectite group clays are used to synthesize nanoclays. Most often, montmorillonite clay is used to prepare those vehicles because the surface's negative charges enable cations to exchange, resulting in the creation of a superior carrier for plant nutrients. In addition, nanoclays have appropriate slow-release qualities that match the clay's high aspect ratio. There has been some research into the modification of nanoclay in order to develop slow release fertilizers such as zinc oxide [18], nitrogen fertilizers [5], and urea [33]. Despite the fact that this is an emerging field, this technology has the potential to develop plant nutrient use efficiency to a very high level.

5.2 Nanopesticides

Pesticides are a class of chemicals that eliminate plant unwanted pests. The main issue with pesticides is their low solubility and persistence. Due to these factors, the efficiency of pesticides is low, necessitating the use of ample quantities to achieve acceptable results. Pesticide overuse is harmful to the environment because it has the potential to wipe out beneficial insects as well. Nanopesticides will be extremely beneficial to the industry in this situation [29]. There are few types of nanopesticides on the market today, including nanosilver, nanocopper, and nanogold-based nano pesticides, [31], mesoporous silica-based nanomaterials [23], polymeric nanoparticles, iron oxide nanoparticles, carbon-based nanocarriers, and nanoclay pesticides [64]. Among them, nanoclay-based pesticides are commonly used because it controls the insect pests, acting by physisorption through insect cuticular lipids. Nanoclay gut busters are another type of functional nanoinsecticide with controlled release of the contents when exposed to an alkaline environment such as an insect stomach [30]. Nano-clay is seen as a material that is good for the economy and better for making multifunctional nano-carrier materials for pesticides.

Controlled release of nanoclay pesticides was engineered by surface coating with different types of polymers, which played a significant role in the modification of electrostatic interaction between the chemical load and clay particles such as bentonite and kaolinite. Recent research described how a nano-encapsulated pesticide formulation with slow-releasing properties and better solubility, permeability, and stability could be made [49]. It has been shown that the effect of organophilic silane on smectite clay can be used to test their ability to detect organophilic pesticides through electrochemistry [34]. The development of nanoclay application technology for pesticides will open up a wide range of opportunities for the industry in terms of managing diseases and pests in the future.

5.3 Nanoherbicides

Herbicides, also referred to as weedkillers, are chemicals used to manage undesirable plants, or weeds. Non-selective herbicides can be used to clear waste ground, industrial and construction sites, railways, and railway embankments because they kill all plant material with which they come into contact. Selective herbicides control specific weed species while leaving the desired crop relatively unharmed. There are some active herbicides, but they tend to degrade quickly by soil microorganisms and are less soluble in water (REF). The effectiveness of this kind of active ingredient applied to soil depends greatly on two variables: the rate of absorption and the rate of biodegradation. If the dose is not accurately controlled when using weedicides, the entire plant community could be wiped out. However, this risk can be mitigated if the applications are carefully managed. If pesticides are encapsulated, the active ingredient can be controlled release which also minimizes active ingredient degradation [48]. It has been reported that encapsulation increases pesticide efficacy as well as half-life. Therefore, nanoherbicides can be used effectively in this context to solve this major problem [47]. Some nanoherbicides, for instance, contain a combination of herbicides such as atrazine, ametrine, and triazine. There have been reports that nanoweedicides are 80 per cent more effective against a variety of weed species. There is great potential to adopt all types of weedicides at the nanoscale level and bring all of the economic and environmental benefits to the entire world.

6 Toxicity and Environmental Impacts

The toxicity and environmental impact of nanoscale-based formulations are some of the debate areas in the field of nanotechnology. Those concerns fade away with proper scientific experiments, followed by their key findings. But still, there are some arguments that need to be clarified in terms of environmental or bioaccumulation of nano-clay base fertilizers, herbicides, and pesticides in soil, surface water, and groundwater, at the same time potential impacts on non-target organisms. Similarly, it has been reported that most of the efficacy of the nono-bind active ingredient depends on environmental factors, such as pH, ionic strength, and dissolved molecules [24]. Therefore, the targeted nano-clay base nutrient composite can be modified organically, inorganically, and polymer-wise to circumvent this problem. Alternatively, these nano-clays would be able to release the nutrients from the vehicle in a slow or controlled manner [42].

Clay minerals contain a variety of positive charges, which is advantageous for crop and soil enhancement. Nanoclay toxicity is likely influenced by particle size, clay composition, compounds used to intercalate, low solubility at low pH, surface reactivity, hydrophobicity, and duration of exposure to the particles, among other variables [63]. In numerous instances, the majority of nanoclay materials are toxic, but the level of toxicity is dependent on the biological application. In terms of application, nanoclays are safer than other nanocomposites [40]. These nanoclays have demonstrated specific toxicity in a number of instances, the majority of which are associated with their organic functionalization [43]. Most importantly to test the toxicity of the rage of nanoclay materials, different types of organisms used including *Paramecium caudatum protozoan*, *Selenastrumcapricornutum alga*, *Ceriodaphniadubia flea*, and the juvenile eastern rainbow fish [9]. These findings also shed light on potential applications of nano clay for the development of weedicides, pesticides, and fertilizers.

It has been reported that nanoclays pose very low risks to soil and environmental toxicity; however, the quaternary, ammonium compounds, an organic molecule commonly used in the synthesis of organoclays, pose significant toxicity to living organisms, including soil microorganisms [36]. These types of ammonium compounds are hydrophobic in nature. The final nano-clay system would be the adsorbents of many organic and inorganic pollutants, which could lead to a major environmental problem [7]. These organic modifications are carried out because of their high reactivity, low cost, and availability. The application of these types of organic nanoclay systems into the environment would inhibit soil metabolic activity and destroy the viability of important bacteria [56]. The majority of the non-clay has settled on the soil's surface, where microorganisms are abundant and have a significant impact on the physical and chemical characteristics of the soil. Parallelly, the application of organoclay to agricultural soils may modify soil bacterial communities via chemical and physical actions [50]. The in *vivo* studies of nanotoxicity in plants and soil could be given priority [65]. Concerning the toxicity mechanisms in terms of using nanoclay materials, cell death, geno-toxicity, mutagenicity, and oxidative stress have been reported elsewhere. However, the majority of studies have primarily relied on in vitro bioassays, which gives researchers the chance to draw a clear conclusion about the toxicity of nanoclay in in vivo systems [20]. Studies on the long-term effects of nanofertilizers, pesticides, and weedicides on bioaccumulation, long-term persistence in the plant, as well as transportation through the food chain, are extremely scarce. All of these findings point to the necessity of conducting extensive research in order to determine whether or not the materials used are safe for long-term use and whether or not the harvest generated is safe for long-term human consumption.

7 Conclusion and Future Perspectives

In conclusion, the era of nanotechnology is rapidly emerging, and its applications in sustainable agriculture will become widespread. The application of nanotechnology has resulted in significant improvements in the agricultural industry, particularly in the fields of fertilizer, weedicide, pesticide, and disease control. This comes at a very opportune time given the widespread and well-documented abuse of agricultural chemicals all over the world. On other hand, the overuse of agrochemicals to boost agricultural production has resulted in the pollution of both the topsoil system and the groundwater system and subsequently food. Increase agricultural productivity is essential, but it should be made to minimize their impact on the natural environment and human health. Nevertheless, there are numerous facets of nanotechnology that have not yet been explored, and there is an urgent to explore fundamental nature of how these materials work on biological systems. The use of nanoclay materials for the delivery of nutrients is expected to reduce the dosage and ensure controlled release. There are both beneficial and negative effects of using nanofertilizers, insecticides, and weedicides; thus, they should all be properly studied prior to recommendation. After a brief summary of what has been done with nanofertilizers, nanopesticides, or nanoweedicides over the last ten years, it is important to take into account the views of scientific, industrial, and regulatory experts.

References

1. Al-Ani, T., Sarapää, O.:Clay and clay mineralogy. Geochemical Survey of Finland (September), pp. 1–91 (2008)
2. Avila-Quezada, G.D., et al.: Strategic applications of nano-fertilizers for sustainable agriculture: benefits and bottlenecks. Nanotechnol. Rev. **11**(1), 2123–2140 (2022). https://doi.org/10.1515/ntrev-2022-0126
3. Awasthi, A., Jadhao, P., Kumari, K.: Clay nano-adsorbent: structures, applications and mechanism for water treatment. SN Appl. Sci. **1**(9) (2019). https://doi.org/10.1007/s42452-019-0858-9
4. Bagherifam, S., et al.: Highly selective removal of nitrate and perchlorate by organoclay. Appl. Clay Sci. **95**, 126–132 (2014). https://doi.org/10.1016/j.clay.2014.03.021
5. Bauli, C.R., et al.: Eco-friendly carboxymethyl cellulose hydrogels filled with nanocellulose or nanoclays for agriculture applications as soil conditioning and nutrient carrier and their impact on cucumber growing. Colloids Surf., A **623**, 126771 (2021). https://doi.org/10.1016/j.colsurfa.2021.126771
6. Bh, S., et al.: Modified nano-clay formulation and their application. Int. J. Chem. Stud. **6**(4), 705–710 (2018)
7. Bhat, K.U., Bhat Panemangalore, D.: Microbes–Surfaces interactions BT—Application of microbes in environmental and microbial biotechnology. In: Inamuddin, Ahamed, M.I., Prasad, R. (eds.) Springer Nature Singapore, Singapore, pp. 473–499 (2022). https://doi.org/10.1007/978-981-16-2225-0_16
8. Binat, Z.: Analysis results and modification of Na+-montmorillonite with quarterner ammonium salt **7**(9), 735–740 (2016)
9. Blinova, I., et al.: 'Potential hazard of lanthanides and lanthanide-based nanoparticles to aquatic ecosystems: data gaps, challenges and future research needs derived from bibliometric analysis. Nanomaterials (2020). https://doi.org/10.3390/nano10020328
10. Calicioglu, O., et al.: The future challenges of food and agriculture: an integrated analysis of trends and solutions. Sustainability (Switzerland) **11**(1) (2019). https://doi.org/10.3390/su11010222.
11. Cardinaud, G., et al.: Calcined clay—Limestone cements: hydration processes with high and low-grade kaolinite clays. Constr. Build. Mater. **277**, 1–27 (2021). https://doi.org/10.1016/j.conbuildmat.2021.122271
12. Celoria, G., et al.: Silica particles derived from natural Kaolinite for the removal of Rhodamine B from polluted water. Processes **10**(5), 1–15 (2022). https://doi.org/10.3390/pr10050964
13. Chand Mali, S., Raj, S., Trivedi, R.: Nanotechnology a novel approach to enhance crop productivity. Biochem. Biophys. Reports **24**, 100821 (2020). https://doi.org/10.1016/j.bbrep.2020.100821
14. Chen, L., et al.: Role of Montmorillonite, Kaolinite, or Illite in pyrite flotation: differences in clay behavior based on their structures. Langmuir **36**(36), 10860–10867 (2020). https://doi.org/10.1021/acs.langmuir.0c02073
15. Cheng, K., Heidari, Z.: A new method for quantifying cation exchange capacity in clay minerals. Appl. Clay Sci. **161**(May), 444–455 (2018). https://doi.org/10.1016/j.clay.2018.05.006
16. Churchman, G.J., et al.: Clay minerals as the key to the sequestration of carbon in soils. Clays Clay Miner. **68**(2), 135–143 (2020). https://doi.org/10.1007/s42860-020-00071-z
17. Datta, R., Swaroop, R.: Soil carbon stabilization to mitigate climate change, soil carbon stabilization to mitigate climate change (2021). https://doi.org/10.1007/978-981-33-6765-4
18. Dubey, A.N., Chattopadhyaya, N., Mandal, N.: Variation in soil microbial population and soil enzymatic activities under zincated nanoclay polymer composites (ZNCPCs), Nano-ZnO and Zn solubilizers in rice rhizosphere. Agric. Res. **10**(1), 21–31 (2021). https://doi.org/10.1007/s40003-020-00488-x
19. Fertahi, S., et al.: Recent trends in organic coating based on biopolymers and biomass for controlled and slow release fertilizers. J. Contr. Release **330**, 341–361 (2021). https://doi.org/10.1016/j.jconrel.2020.12.026

20. Gmoshinski, I.V., et al.: Nanoclays in food products: benefits and possible risks (literature review). Health Risk Anal. **1**, 142–164 (2020). https://doi.org/10.21668/health.risk/2020.1.16.eng
21. Guha, T., et al.: Nanocomposites for delivering agrochemicals: a comprehensive review. J. Agric. Food Chem. **68**(12), 3691–3702 (2020). https://doi.org/10.1021/acs.jafc.9b06982
22. Guo, H., et al.: Nano-enabled fertilizers to control the release and use efficiency of nutrients. Curr. Opinion Environ. Sci. Health **6**, 77–83 (2018). https://doi.org/10.1016/j.coesh.2018.07.009
23. Hajji-Hedfi, L., Chhipa, H.: Nano-based pesticides: challenges for pest and disease management. Euro-Mediterr. J. Environ. Integr. **6**(3), 69 (2021). https://doi.org/10.1007/s41207-021-00279-y
24. Hamid, Y., et al.: Sepiolite clay: a review of its applications to immobilize toxic metals in contaminated soils and its implications in soil–plant system. Environ. Technol. Innov. **23**, 101598 (2021). https://doi.org/10.1016/j.eti.2021.101598
25. Hemdan, N.A., Hussein, M.M., El-ashry, S.: Conventional and nano fertilizers and its effect on growth and nutrient status of lupine plants. Curr. Sci. Int. **9**(4), 698–705 (2020). https://doi.org/10.36632/csi/2020.9.4.63
26. Huggett, J.M.: Clay minerals. In: Encyclopedia of Geology, (i), pp. 358–365 (2004). https://doi.org/10.1016/B0-12-369396-9/00273-2
27. Hwang, J., Pini, R.: Supercritical CO2 and CH4 uptake by Illite-Smectite clay minerals. Environ. Sci. Technol. **53**(19), 11588–11596 (2019). https://doi.org/10.1021/acs.est.9b03638
28. Jawaid, M., Qaiss, A. el K., Bouhfid, R.: Nanoclay reinforced polymer composites: nanocomposites and bionanocomposites. Eng. Mater. (2016).https://doi.org/10.1007/978-981-13-9833-9
29. Kah, M., et al.: A critical evaluation of nanopesticides and nanofertilizers against their conventional analogues. Nat. Nanotechnol. **13**(8), 677–684 (2018). https://doi.org/10.1038/s41565-018-0131-1
30. Kanel, S.R., et al.: Chapter 12—Assessment of health, safety, and economics of surface-modified nanomaterials for catalytic applications: a review. In: Gawande, M.B., Mustansar Hussain, C., Yamauchi, Y.B.T.-S.M.N. for A. in C. (eds.) Micro and Nano Technologies. Elsevier, pp. 289–317 (2022). https://doi.org/10.1016/B978-0-12-823386-3.00009-X
31. Kapinder, Dangi, K., Verma, A.K.: Efficient & eco-friendly smart nano-pesticides: emerging prospects for agriculture. Mater. Today: Proc. **45**(April), 3819–3824 (2020).https://doi.org/10.1016/j.matpr.2021.03.211
32. Keskinen, R., et al.: Mineral composition and its relations to readily available element concentrations in cultivated soils of Finland. Acta Agric. Scand. Sect. B Soil Plant Sci. **72**(1), 751–760 (2022). https://doi.org/10.1080/09064710.2022.2075790
33. Kirti, S., et al.: Mitigating nitrous oxide emission using nanoclay-polymer composites in rice-wheat cropping system. Archiv. Agron. Soil Sci. **67**(4), 459–473 (2021). https://doi.org/10.1080/03650340.2020.1735629
34. Kumar, S., et al.: Nano-based smart pesticide formulations: emerging opportunities for agriculture. J. Control. Release **294**(November 2018), 131–153 (2019). https://doi.org/10.1016/j.jconrel.2018.12.012
35. Lawrencia, D., et al.: Controlled release fertilizers: a review on coating materials and mechanism of release. Plants **10**(2), 1–26 (2021). https://doi.org/10.3390/plants10020238
36. Lazzara, G., Massaro, M., Riela, S.: Current status of nanoclay phytotoxicity BT—Phytotoxicity of nanoparticles. In: Faisal, M., et al. (eds). Springer International Publishing, Cham, pp. 151–174 (2018). https://doi.org/10.1007/978-3-319-76708-6_6
37. de Macedo Neto, J.C., et al.: Kaolinite review: intercalation and production of polymer nanocomposites. Eng. Sci. **17**, 28–44 (2022). https://doi.org/10.30919/es8d499
38. Marella, S., Nirmal Kumar, A.R., Tollamadugu, N.V.K.V.P.: Nanotechnology-based innovative technologies for high agricultural productivity: opportunities, challenges, and future perspectives. In: Recent Developments in Applied Microbiology and Biochemistry (June), pp. 211–220 (2021). https://doi.org/10.1016/b978-0-12-821406-0.00019-9

39. Maurya, P.K., et al.: High resolution 3D subsurface mapping using a towed transient electromagnetic system—tTEM: case studies. Near Surf. Geophys. **18**(3), 249–259 (2020). https://doi.org/10.1002/nsg.12094
40. Mazari, S.A., et al.: Nanomaterials: applications, waste-handling, environmental toxicities, and future challenges—A review. J. Environ. Chem. Eng. **9**(2), 105028 (2021). https://doi.org/10.1016/j.jece.2021.105028
41. Merino, D., et al.: Nanoclay as carriers of bioactive molecules applied to agriculture. In: Handbook of Nanomaterials and Nanocomposites for Energy and Environmental Applications, pp. 1–22 (2020). https://doi.org/10.1007/978-3-030-11155-7_62-1
42. Merino, D., et al.: Nanoclay as carriers of bioactive molecules applied to agriculture BT—Handbook of nanomaterials and nanocomposites for energy and environmental applications. In: Kharissova, O.V., Torres-Martínez, L.M., and Kharisov, B.I. (eds.) Springer International Publishing, Cham, pp. 433–453 (2021). https://doi.org/10.1007/978-3-030-36268-3_62
43. Messa, L.L., Souza, C.F. Faez, R.: Spray-dried potassium nitrate-containing chitosan/montmorillonite microparticles as potential enhanced efficiency fertilizer. Polym. Test. 106196 (2019). https://doi.org/10.1016/j.polymertesting.2019.106196
44. Mohammed, I., et al.: Mineral Surface Chemistry, pp. 1–20 (2022)
45. de Moraes, A.C.P., et al.: The potential of nanomaterials associated with plant growth-promoting bacteria in agriculture. 3 Biotech **11**(7) (2021). https://doi.org/10.1007/s13205-021-02870-0
46. Muhammed, N.S., Olayiwola, T., Elkatatny, S.: A review on clay chemistry, characterization and shale inhibitors for water-based drilling fluids. J. Petrol. Sci. Eng. **206**(May), 109043 (2021). https://doi.org/10.1016/j.petrol.2021.109043
47. Nadiminti, P.P., et al.: Use of Mg-Al nanoclay as an efficient vehicle for the delivery of the herbicide 2,4-Dichlorophenoxyacetic Acid. ACS Sustain. Chem. Eng. **7**(12), 10962–10970 (2019). https://doi.org/10.1021/acssuschemeng.9b02001
48. Neme, K., et al.: Application of nanotechnology in agriculture, postharvest loss reduction and food processing: food security implication and challenges. Heliyon **7**(12), e08539 (2021). https://doi.org/10.1016/j.heliyon.2021.e08539
49. Nuruzzaman, M., et al.: Capability of organically modified montmorillonite nanoclay as a carrier for imidacloprid delivery. ACS Agric. Sci. Technol. **2**(1), 57–68 (2022). https://doi.org/10.1021/acsagscitech.1c00125
50. Olagoke, F.K., et al.: Importance of substrate quality and clay content on microbial extracellular polymeric substances production and aggregate stability in soils. Biol. Fertil. Soils **58**(4), 435–457 (2022). https://doi.org/10.1007/s00374-022-01632-1
51. Pereira, A.D.E.S., et al.: Nanotechnology potential in seed priming for sustainable agriculture. Nanomaterials **11**(2), 1–29 (2021). https://doi.org/10.3390/nano11020267
52. Perelomov, L., et al.: The synthesis of organoclays based on clay minerals with different structural expansion capacities. Minerals **11**(7), 1–15 (2021). https://doi.org/10.3390/min11070707
53. Pratt, C., et al.: Geo-agriculture: reviewing opportunities through which the geosphere can help address emerging crop production challenges. Agronomy **10**(7) (2020). https://doi.org/10.3390/agronomy10070971
54. Rani, K., et al.: Bio-activation of waste mica through potassium solubilizing bacteria and rice residue. Indian J. Agric. Sci. **92**(1), 75–79 (2022). https://doi.org/10.56093/ijas.v92i1.120843
55. Sadati Valojai, S.T., et al.: Response of rice yield and quality to nano-fertilizers in comparison with conventional fertilizers. J. Plant Nutr. **44**(13), 1971–1981 (2021). https://doi.org/10.1080/01904167.2021.1884701
56. Schulz, M., Manies, K.: Biofilms in the critical zone: distribution and mediation of processes BT—Biogeochemistry of the critical zone. In: Wymore, A.S., et al. (eds.) Cham: Springer International Publishing, pp. 89–119 (2022). https://doi.org/10.1007/978-3-030-95921-0_4
57. Shah, V., Scott, A.: Use of kaolinite clays in development of a low carbon MgO-clay binder system. Cem. Concr. Res. **144**(March), 106422 (2021). https://doi.org/10.1016/j.cemconres.2021.106422

58. Shakiba, S., et al.: Emerging investigator series: polymeric nanocarriers for agricultural applications: synthesis, characterization, and environmental and biological interactions. Environ. Sci. Nano **7**(1), 37–67 (2020). https://doi.org/10.1039/c9en01127g
59. Singh, R.P., Handa, R., Manchanda, G.: Nanoparticles in sustainable agriculture: an emerging opportunity. J. Control. Release **329**, 1234–1248 (2021). https://doi.org/10.1016/j.jconrel.2020.10.051
60. Sivarethinamohan, R., Sujatha, S.: Unlocking the potentials of using nanotechnology to stabilize agriculture and food production. In: AIP Conference Proceedings, 2327(February) (2021). https://doi.org/10.1063/5.0039418
61. Taylor, P., et al.: Organophilic nano clay: a comprehensive review organophilic nano clay : a comprehensive review. Trans. Indian Ceram. Soc. **2013**, 37–41 (2013)
62. Underwood, T.R., Bourg, I.C.: Large-scale molecular dynamics simulation of the dehydration of a suspension of smectite clay nanoparticles. J. Phys. Chem. C **124**(6), 3702–3714 (2020). https://doi.org/10.1021/acs.jpcc.9b11197
63. Vejan, P., et al.: Controlled release fertilizer: a review on developments, applications and potential in agriculture. J. Control. Release **339**, 321–334 (2021). https://doi.org/10.1016/j.jconrel.2021.10.003
64. Vijayakumar, M.D., et al.: Evolution and recent scenario of nanotechnology in agriculture and food industries. J. Nanomater. (2022). https://doi.org/10.1155/2022/1280411
65. Yilmaz, B., et al.: Synthesis, characterization and biological properties of intercalated Kaolinite nanoclays: intercalation and biocompatibility. Adv. Mater. Sci. **19**(1), 83–99 (2019). https://doi.org/10.2478/adms-2019-0007
66. Zhang, L., et al.: Review{\textemdash}clay mineral materials for electrochemical capacitance application. J. Electrochem. Soc. **168**(7), 70558 (2021). https://doi.org/10.1149/1945-7111/ac163b
67. Zhao, L., et al.: Nano-Biotechnology in agriculture: use of nanomaterials to promote plant growth and stress tolerance. J. Agric. Food Chem. **68**(7), 1935–1947 (2020). https://doi.org/10.1021/acs.jafc.9b06615

The Environmental Toxicity of Halloysite Clay and Its Composites

Mingxian Liu, Jiawei Huang, and Ming Huang

Abstract The extensive use of clay nanomaterials causes a rise in the amount of nanoparticles released into the environment. It is essential to determine the phytotoxicity of the nanoclays, such as tubular like halloysite nanotubes (HNTs) and rod-like attapulgite. HNTs show unique empty lumen structure with different outer/inner surface chemical composition. HNTs range in length from 100 to 2000 nm and in diameter from 20 to 80 nm. Industrial products based on HNTs are rapidly developing due to their good mechanical, thermal, and biological properties. HNTs were discovered to be capable of entering plant roots and promoting wheat growth, while also improving the accumulation of biomass and secondary metabolites in tobacco cells. Furthermore, the uptake of the HNTs with different surface functional groups by animal or human cells has been found. With the use of mice, *Caenorhabditis elegans*, and zebrafish models, the in vivo toxicity of the HNTs was also evaluated. These results are significant for the development of HNT applications in a variety of fields, including waste management and environmental protection, as well as their potential for regulating active chemical release and biomedicine area.

Keywords Nanotube · Modification · Cytotoxicity · Uptake · Plant

1 Introduction

The number of nanoparticles emitted into the environment gradually increased as industrial applications advanced. Nanomaterials could interact with plants, microorganisms and soil, accumulating in plant tissues and influencing plant growth, which increases the potential risk to human health via the food chain. Therefore, it is critical to comprehend the reaction of plant to nanoparticle exposure, which has the potential to open up new horizons in agricultural development and food safety.

M. Liu (✉) · J. Huang · M. Huang
Department of Materials Science and Engineering, College of Chemistry and Materials Science,
Jinan University, Guangzhou 510632, P.R. of China
e-mail: liumx@jnu.edu.cn

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research
and Technology, https://doi.org/10.1007/978-981-99-2544-5_27

Halloysites clay nanotubes (HNTs), the chemical formula of $Al_2Si_2O_5(OH)_4 \cdot nH_2O$, are a kind of natural one-dimensional clay with a high aspect ratio and a hollow lumen structure[1]. The length, inner diameter, and outer diameter h of HNTs range 100–2000 nm, 10–30 nm, and 30–50 nm, respectively. The inner surfaces of HNTs mainly consist of aluminoxane (Al–OH) groups with positive charge, and the external surfaces are composed of silicon-oxygen (Si–O) groups with negative charge. Due to their great absorption capacity and excellent biocompatibility, HNTs are commonly utilized as waste adsorbents, biomaterials for tissue engineering, and drug delivery carriers. HNTs have the power to enhance cell affinities, mechanical characteristics, and capacity for drug loading of biomaterials. The toxicity of HNTs in vitro and in vivo to various cells and animals has been extensively investigated, and the results show that HNTs have good biosafety [2]. HNTs have recently been used as pesticide and fertilizer transporters. Before application, the impact of the HNTs on the plant seed germination and growth and the related environmental toxicity should be fully assessed. The toxicity of nanoparticles depends on particle size, chemical composition, surface properties, morphology, and impurities content in the nanoparticles.

With the industrial application of HNT, its ecological and environmental safety deserves further attention. In this chapter, we reviewed the recent advances of toxicity research results of HNTs toward different plant and animal models (Fig. 1).

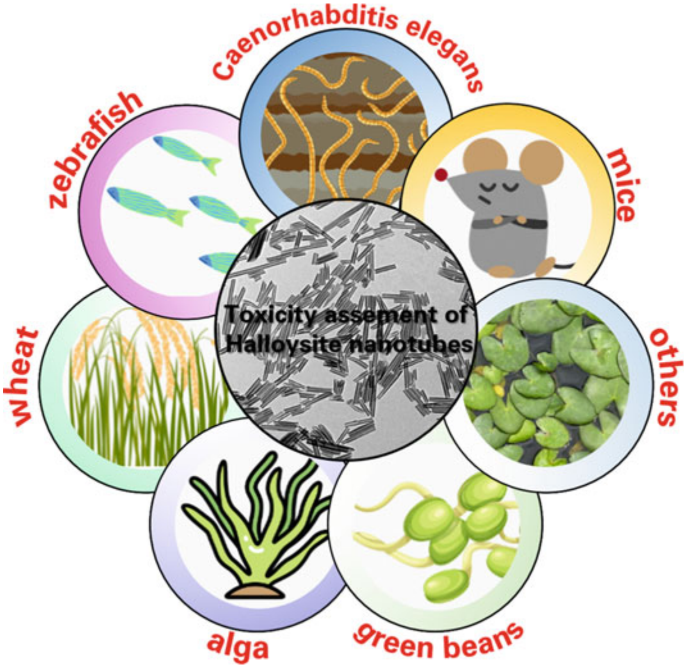


Fig. 1 Toxicity of halloysite toward different models

2 Toxicity of Halloysite Toward Wheat

Wheat was used as a plant model to study the phytotoxicity of raw HNTs [3]. The plant growth and germination rate of wheat treated with HNTs were measured. The effects of HNTs on oxidative damage index, biomass (including fresh weight, root length, and stem length) and chlorophyll content were studied in detail. The plant cytotoxicity of HNTs was then evaluated by tobacco callus cells. All of the data demonstrated that HNTs can stimulate wheat development at low concentrations (0.10 mg/mL) but suppress it at large concentrations (100 mg/mL). Plant development is stimulated by the addition of silicon elements from HNTs, but plant growth is suppressed by the clogging of the pore structure by excessive concentrations of HNTs. This study extended the comprehension of the interactions between HNTs and plants, which promotes the development and application of HNTs in the environmental protection and agricultural field.

2.1 *Characterization of the Raw HNTs*

Before measuring phytotoxicity, the morphology and structure of HNTs should be determined. HNTs have characteristic tubular shapes with hollow lumen and sharp, smooth walls. HNTs have diameters ranging from 50 to 70 nm and lengths ranging from 100 to 1000 nm. The AFM scans show that HNTs have a smooth and consistent tube shape. HNTs have diffraction peaks at 12°, 20°, and 25°, which correspond to the (001), (020,110), and (002) planes, respectively. There are no peaks of impurities (such as quartz and alunite). HNTs show characteristic absorption peaks at 3623 and 3695 cm^{-1}, which are attributed to the inner hydroxyl groups and O–H stretching of inner-surface hydroxyl groups, respectively. The particle size distribution of purified HNTs is narrow, with an average particle size of 249.3 nm. The zeta potential of HNTs is -14.6 mV, suggesting satisfied dispersion stability of HNTs in water. The homogeneous tubular shape and excellent purity of HNTs assure the biological data's dependability and reproducibility.

2.2 *Effect of HNTs on Wheat Germination and Growth*

Wheat seedlings were put in petri plates with HNTs dispersion of various concentrations or deionized water as a control to investigate if HNTs may affect plant germination and growth. HNTs show no discernible influence on wheat germination and total height at different culture times compared to the control group. Wheat seeds germinated and grew well in all groups, including the high HNTs concentration group. HNTs, on the other hand, have a major impact on the roots. The low concentration of HNTs promotes root development, but high concentration of HNTs (100 mg/mL) limits root length.

The results show that GP for all groups is near 100%, and the germination rate of wheat seeds containing HNTs is not substantially different from that of the control group. This indicates that HNTs have no significant influence on wheat seed germination, even at a high concentration of 100 mg/mL. The biomass was then measured at 3, 5, and 7 days to investigate the effect of HNTs on the growth of wheat seedlings. In comparison with the control, the biomass of wheat seedlings germination and growth in petri dishes was considerably higher at low HNTs concentrations (0.1, 1, and 10 mg/mL) and decreased at high HNTs concentrations (100 mg/mL). Seedlings in petri dishes containing HNTs (0.1, 1, and 10 mg/mL) had 1.2, 1.35, and 1.05 times the root length of control seedlings at 7 days, while seedlings in high concentrations of HNTs (100 mg/mL) had 56.4% less root length compared to the control. This shows that high concentrations of HNTs suppress root growth by filling the pores at the root surfaces. In terms of shoot length, low concentrations of HNTs has a beneficial effect and promotes shoot growth. The fresh weight of wheat seedlings containing HNTs (1 mg/mL) increased by 17.4% at 7 days compared with seedlings in the control group, but seedlings with high concentrations of HNTs (100 mg/mL) decreased by 6.5% compared with the control group. Thus, the concentration of HNTs affected the germination and growth of wheat. At relatively low doses of HNTs (below 10 mg/mL), no symptoms of toxicological effects were observed in wheat plants. High concentrations of HNTs inhibited shoot growth on 3 and 5 day, but the shoot length of the group with high concentrations of HNTs is equivalent to that of the control at 7 days. At 7 days, the fresh weight of wheat seedlings containing HNTs (1 mg/mL) rose by 17.4% compared to seedlings produced in the control group, whereas seedlings in the high concentration of HNTs (100 mg/mL) declined by 6.5%. As a result, the concentration of HNTs influences wheat germination and growth. No toxicological effects were seen in the wheat plants at low doses of HNTs (less than 10 mg/mL).

2.3 Effect of HNTs on Root Development and Leave Size

Nanoparticles can be deposited on the surfaces of plant root tips, reducing the capacity of plants to absorb nutrients and water. The effect of HNTs on root morphology was then studied. Compared to the control group, the root diameter of wheat seedlings cultivated in different doses of HNTs (0.1, 1, 10, 100 mg/mL) rises by 30, 38, 40, and 56.8%. The development of root hairs is thought to be an adaptive response to nanoparticle deposition. Root hairs can improve root absorption area; hairs are polarized outgrowths of root epidermal cells, and their start and development (elongation) are regulated by various sets of genes and are hormonally sensitive. When HNTs are added to the culture media, the growth environment becomes one of water scarcity and drought. The adaptive response of wheat enhanced the length and diameter of HNTs-treated wheat groups. Additionally, the groups treated by HNTs have more root hairs than the control group (data not shown). TiO_2 and CuO nanoparticles, among others, may also be able to encourage the growth of root hair. At 7 days, the half-leaf width of wheat treated with different concentrations of HNTs increases marginally as compared to the control group. Increased leaf size is important for photosynthetic room growth. Overall, HNTs can enhance wheat development at a specific concentration while exhibiting minor phytotoxicity at a higher dose.

2.4 Effect of HNTs on Chlorophyll and Oxidative Damage Index

Chlorophyll absorbs sunlight energy, which a plant needs to generate food, and it plays a crucial function in keeping plants green and healthy. Chlorophyll a is the primary photosynthetic pigment in plants, whereas chlorophyll b is a common auxiliary pigment. The chlorophyll a/b concentration ratio regulates the amount of light absorbed. Because chlorophyll is essential for metabolic activities, a rise in chlorophyll concentration or a/b content ratio may pose issues for plants. HNTs can affect plant growth and chlorophyll synthesis by entering the plant via the uptake process during water transport. The chlorophyll content of wheat seedlings increased after treatment with certain concentrations HNTs. For example, the chlorophyll content of the 1 mg/mL group is 13%, which is higher than that of the control seedlings. Within a certain concentration of HNTs, the ratio of chlorophyll a/b in seedlings treated with HNTs is somewhat lower than in the control group. The ratio of chlorophyll a/b is larger in the high-concentration HNTs than in the control group. The chlorophyll a/b concentration ratio regulates the intensity of absorbed light. Plants have an adaptation response at higher content ratios, which limits the chloroplast from optimizing light-collecting capabilities, resulting in a shift in photosynthetic electron transport capacity. As a result, high HNTs concentrations may impair plant photosynthetic electron transmission capability, photosynthesis, and light absorption. When the concentration of chitosan nanoparticles was 10 ppm, the chlorophyll content of coffee chlorophyll increased from 30 to 60%, and as the concentration increased to 20–50 ppm, the chlorophyll content decreased. This conclusion of research is consistent with our study.

Oxidative stress may be responsible for the toxicity of HNTs to plants. Therefore, a series of oxidative damage indices (H_2O_2 content, cell membrane permeability, and malondialdehyde MDA content) were measured. Wheat seedlings with lower concentrations of HNTs had lower ELI and H_2O_2 levels than the control group, whereas seedlings with high concentrations of HNTs (100 mg/mL) had greater ELI and H_2O_2 contents than the control group. Low doses of HNTs had a slight effect on the electrolytes of the seedlings and reduced the leakage of active oxygen species. MDA is regarded as a generic marker of lipid peroxidation. Seedlings produced from seeds exposed to modest dosages of HNTs (0.1–1 mg/mL) had a lower MDA content. However, high-dose HNTs increased ROS, electrolyte leakage, and MDA levels, indicating that cell membrane stability is compromised. It is understood that plant tissues may be shielded against osmotic stress by the structural integrity of cell membrane. Thus, whereas high-dose HNTs could diminish cell membrane stability and hinder wheat development, low-dose HNTs were able to stabilize cell membrane and increase wheat growth.

2.5 Uptake and Transport of HNTs by Wheat Root

Crops may absorb nanoparticles through foliar or root absorption, which raises safety issues. It has been extensively noted that diverse animal cells can absorb HNTs. However, there have only been a few reports of HNTs entering plants up to this point. The pictures of wheat seedling roots that have been cultured in Rhodamine B-labeled HNTs solutions can be detected by using the fluorescence microscope. It was easy to see the red fluorescence signals with some aggregated patches, which were the Rhodamine B-labeled HNTs. The red-light intensities rise as the HNT level rises, indicating that HNTs may reach the wheat root. SEM images of root cross-sections were examined to validate the presence of HNTs in the root. The absence of HNTs in the control group is obvious, however HNTs are identified in the cortex of roots cultivated in HNTs dispersion. HNTs in the root aggregated together and the amount of aggregation increased with increasing HNTs loading. The aggregation phenomenon of HNTs in plants is caused by the changed ions concentrations, as plant cells contain various ions such as K^+ and Na^+. The aggregated HNTs stick to the walls of the plant pores, and the aggregation of HNTs has an influence on plant development that can be negative or favorable. The chemical makeup of HNTs includes silicon, and silicon is a helpful ingredient for plant growth, such as boosting drought tolerance and crop quality and production. It is probable that the introduction of silicon element via HNTs boosts the biomass of wheat seedlings in HNTs-treated groups. The amount of HNTs entering the roots rises as the concentration of the HNTs dispersion increases. The large accumulation of nanotubes on the root surface following the treatment of wheat with high concentration may impede water transport and water use efficiency in the root system, lowering transpiration and impairing plant growth and development. And no HNTs were found in the xylem of any of the samples. The plant root cap is generally protected by the boundary cell mucus layer, which is made up of negatively charged root fluids. Since HNTs have negatively charged Si–O–Si groups on their exterior surfaces, so they will not absorb mucus at the root border and can penetrate the interior. Aluminum content increases with HNTs concentration in the wheat root, and aluminum is widely considered to be deleterious to plant development. As a result, the effect of HNTs on wheat growth yields a complete outcome, as shown above.

In higher plants, nanoparticles have two primary root absorption and transport pathways: the apoplast transport system and the symbiotic pathway. As HNTs are not found in the xylem, the apoplast route may be responsible for HNT absorption and transport in the roots. HNTs can move across the intercellular space without passing through the cell membrane by first penetrating the cell wall pores and then diffusing into the gap between the cell wall and the plasma membrane. Plant cell wall is a semi-permeable barrier that regulates material transport through pores, and the size of nanoparticles influences whether they may reach plant roots.

3 Toxicity of Halloysite Toward Alga

The biological impacts of HNTs in aquatic ecosystems were also studied on model freshwater alga *Chlorella vulgaris* at cellular, subcellular levels, and tissue [4]. The effects were also compared to those of HNTs' main ingredients nAl_2O_3, $nSiO_2$, and a mixture of $nSiO_2$ and nAl_2O_3.The results showed that these nanomaterials inhibited algal growth in a dose-dependent manner and the inhibition capacity followed the trend of $nAl_2O_3 > \text{HNTs} \approx nSiO_2 + nAl_2O_3 > nSiO_2$. However, HNT treatment produced more reactive oxygen species (ROS) than the $nSiO_2 + nAl_2O_3$ combination without causing substantial changes in enzyme activity. The concept that the nano-tubular shape of HNTs degraded membrane integrity and promoted ROS overproduction was substantiated by surface and ultrastructural observations coupled with flow cytometry. The examination of fatty acid (FA) profiles revealed that an increase in monounsaturated FAs, such as C17:1 and C18:1/n-9, may affect cell membrane fluidity when exposed to HNTs. Cell defense to HNTs could be mediated by the activity of FA desaturase or FA saturation degree. This research sheds new light on the environmental safety of HNTs in aquatic environments.

3.1 HNTs Induced Lower Growth Inhibition but Stronger Oxidative Stress

At doses ranging from 0 to 10 mg/mL, the dose–response associations of algal exposure to HNTs, nAl_2O_3, and $nSiO_2$ were determined. Low concentrations of HNTs exposure (0–1 mg/mL) for 96 h gradually suppressed algal development; however, higher HNTs concentrations from 1 to 10 mg/mL might boost algal stress responses. The EC_{50} of HNTs was determined to be 8.2 mg/mL. By contrast, the calculated 96 h-EC_{50} of $nSiO_2$ and nAl_2O_3 were 12.5 and 0.35 mg/mL, respectively. Interestingly, growth promotion by $nSiO_2$ was detected at low doses of 0.05–1 mg/mL, which probably occurred from nanomaterial stress-response hormesis. Comparison between HNTs (1 mg/mL) and other tested nanomaterials in inhibitory effects on algal growth revealed the following pattern: $nSiO_2 < nSiO_2 + nAl_2O_3 \approx \text{HNTs} < nAl_2O_3$. HNTs exhibited greater inhibition than $nSiO_2$, probably due to $nSiO_2$-induced hormesis or the negative effects of HNT impurities on algae. Unexpectedly, $nSiO_2 + nAl_2O_3$ exhibited similar inhibitory effects as HNTs, which was most likely because abundant $nSiO_2 + nAl_2O_3$ aggregated in algal medium reduced physical contact of $nSiO_2/nAl_2O_3$ with algal cells. Zhao et al. reported that the synthesis of graphene oxidative (GO)-Al_2O_3 hetero aggregates might reduce GO's algal toxicity. In contrast, the $nSiO_2 + nAl_2O_3$ aggregates were unlikely to form under HNT exposure as $nSiO_2$ and nAl_2O_3 were dispersed on the inner and outer surfaces of pristine HNTs, respectively. Thus, HNTs and $nSiO_2 + nAl_2O_3$ may inhibit algal growth through different mechanisms, although they exhibit similar rates of inhibition.

Different interactions between the tested nanomaterials and algal cells were seen in the SEM observation. Due to the presence of Ca bridging in the algal media, HNT exposure caused nanomaterials to adhere to the surface of the algal cells. Additionally, HNT with distinct nano-tubular shape and electrostatic properties might make it easier for their tips to directly penetrate cell membrane, as was seen when carbon nanotubes were exposed to the environment. When exposed to nAl_2O_3, the algal cells became thoroughly coated with the compound. Suggesting the damage could result from electrostatic attraction. When the $nSiO_2$ and nAl_2O_3 co-existed, greater negative charges in $nSiO_2$ than in algae increased the opportunities of nAl_2O_3 interacting with $nSiO_2$ than with algal cells. Therefore, it seems reasonable to believe that the hetero aggregation of $nSiO_2$ and nAl_2O_3 prevented Al_2O_3 from directly contacting algae, resulting in less growth inhibition than exposure to nAl_2O_3 solely. The TEM images further confirmed unlike algal responses to different nanomaterials at ultrastructural levels. HNT exposure damaged cell wall and membrane but remained intact cellular organelles such as chloroplasts. Exposure to nAl_2O_3 or $nSiO_2 + nAl_2O_3$ induced severe cellular damages, such as blurred thylakoids, plasmolysis (red two-way arrow), and reduced plastoglobuli.

The determination of the integrity of algal cell membrane revealed that HNTs caused a higher proportion of membrane-damaged algal cells (77.3%) than any other exposure treatment. The nano-tubular structure of HNTs may be easier to trigger plasma membrane damage via penetration and/or energy-dependent endocytose. Exposure to $nSiO_2$ resulted in damaged membrane and blurred organelles (i.e., starch grana and vacuole) in 23.2% of algal cells. Interestingly, nAl_2O_3 greatly inhibited algal growth but resulted in the lowest ratio of membrane damage (8.2%), suggesting that the transport of nAl_2O_3 to algal cells may be through the release of Al ions rather than the endocytose of nanoscale Al particles. Indeed, our studies indicated that 0.23% Al was liberated from nAl_2O_3, which likely resulted to 76.5% of its inhibition on algal growth. Furthermore, the role of dietary deficiency in nanomaterials-induced algal growth suppression could be ruled out.

In addition to physical damage, exposure to HNTs produced more ROS than any other treatment, suggesting that the balance of cellular homeostasis was disturbed and biological activities of the cell membrane may have been compromised. Induced oxidative stress caused by excessive ROS generation has been identified as a major toxic mechanism for nanomaterials. When the quantity of ROS in the cell surpasses the antioxidant defense capability (i.e., SOD and CAT), lipid peroxidation occurs. The MDA concentration of HNTs-treated algae, on the other hand, did not change substantially from that of the control treatment. The low MDA and high ROS levels showed other antioxidants or pathways that may be involved in cellular protection against excessive ROS in HNTs treatment. In contrast to the control treatment, algae treated with HNTs had higher levels of SOD and CAT. The major antioxidant enzymes, SOD and CAT, are activated to scavenge O_2^- and H_2O_2 for cellular defense and nanomaterial inhibition, respectively. This study indicates that after HNT exposure, the cellular defense was triggered. Although mitotoxicity can be another source of oxidative stress, HNTs exposure had no effect on MMP levels. As a result, HNTs may be able to preserve mitochondrial membrane integrity without triggering mitotoxicity. In contrast, nAl_2O_3 induced severe oxidative stress in algal cells, as evidenced by the highest levels of SOD activity, CAT activity, MDA content, and GSH content, as well as the lowest MMP, despite the fact that intracellular ROS levels in nAl_2O_3 treatment were significantly reduced to the lowest among all treatments. When compared to HNTs, exposure to $nSiO_2 + nAl_2O_3$ caused a large rise in CAT activity, which indicates that $nSiO_2 + nAl_2O_3$ exposure caused an excess of H_2O_2 radicals to be produced and then scavenged by CAT. Additionally, correlation analysis demonstrated that antioxidants were favorably correlated with nanomaterials-induced algal growth suppression, but ROS levels were highly related to the proportion of membrane-damaged algal cells. Oxidative stress and physical contact were thought to be responsible for HNTs-induced membrane damage in this study.

3.2 HNTs Altered FA Compositions of Algal Cells

In addition to the antioxidants indicated above, FAs were shown to be involved in cellular defense against HNT exposure. Fifteen FAs, including four unsaturated fatty acids (UFAs) and ten saturated fatty acids (SFAs), were determined in *C. vulgaris*, with the main components being palmitic acid (C16:0), linoleic acid (C18:2/n-6), α-linolenic acid (C18:3/n-3), oleic acid (C18:1/n-9), and stearic acid (C18:0). The FA profile was consistent with previous studies on FA composition in the same species. Phytotoxicity caused by nanomaterials can generally occur at cell, tissue, and even molecular levels. FA metabolism was discovered to be a significant mechanism in algal response to nanomaterials by metabolomic and transcriptome investigations. Single layer MoS_2 nanosheets treated with humic acid dramatically reduce algal growth inhibition but resulted in the ROS overgeneration, indicating that FAs may play a crucial role in cellular defense against oxidative stress.

It is thought to be a cellular response of algae to nanomaterials, with exposure to HNTs reducing the total amount of PUFAs and UFAs, but significantly increasing the relative amount of SFAs. Mortimer et al. linked decreased total UFAs in nanoscale CuO-exposed protozoa cells to adaptive regulation with stress. More specifically, PUFAs are involved in cell structural function and are vulnerable to contaminants. Under HNTs exposure, the abrupt drop in C18:2/n-6 and C18:3/n-3, as well as the dramatic increase in C16:0 and C18:0, might be attributed to the physical destruction of membrane integrity by the nano-tubular structure. A positive correlation was discovered between ROS and PUFAs levels.

Taken together, HNTs exhibited relatively low inhibitory effects on algal growth, but their nano-tubular structure may enter cells via endocytose and puncture, destruction of cell membrane integrity, and alteration of FA profiles and membrane functions. Unlike $nSiO_2$, nAl_2O_3 and $nSiO_2 + nAl_2O_3$ exposures, HNTs can induce biological responses in algae to protect cells by increasing FA desaturation, whereas antioxidant enzymes may mediate cytoprotection in the former.

3.3 Environmental Implications

As HNTs are progressively used in industry, their environmental impacts and ecological safety need to be better elucidated. Furthermore, changes in the FA profile caused by HNT exposure may have distinct environmental consequences in terms of nutritious food supply and green bioenergy.

The competitiveness of algae as a nutritive food source may be compromised due to exposure to HNT. Since their capacity to offer important FAs for cardiovascular, neurological, and ocular health, algae-derived PUFAs (mostly microalgae) are nutritious and lucrative compounds. Linoleic acid (C18:2/n-6) cannot be synthesized de novo in the body and plays an essential role in dietary supplements as an important PUFA precursor. The possible application of γ-linolenic acid (C18:3/n-9, GLA) largely includes baby formulae for full-term newborns and nutritional supplements. According to our findings, HNT exposure can drastically decrease PUFAs. Therefore, the exposure may cause decreased nutritive values of *C. vulgaris* to probably other organisms in aquatic ecosystems and primary consumers.

HNT exposure, on the other hand, may promote the use of algae as a commercial feedstock for sustainable biofuel. The viability of algae as a commercial feedstock is determined by its lipid production and lipid quality. The latter is strongly linked to FA profiles. For instance, the European Biodiesel Standard EN14212 demands less than 12% of linolenic acid to maintain the balance of oxidative stability. The relative concentration of α-linolenic acid in the control treatment surpassed the biodiesel standard (13.3%), but HNTs-treated algae reduced its proportion to 8.7%. Furthermore, biodiesel with high quantities of oleic acid can reduce cold filter plugging points to adapt to cold conditions, as evidenced by the rise in C18:1/n-9 during HNTs exposure. Therefore, algae with altered FA profiles as a result of HNT exposure might fulfill the quality requirements as a biodiesel feedstock. Thus, the environmental consequences of HNT exposure in aquatic environments should be considered dialectically.

4 Toxicity of Halloysite Toward *Caenorhabditis elegans*

The toxicity of HNTs was assessed using an in vivo model of *Caenorhabditis elegans* (*C. elegans*) [5]. HNTs displayed low toxicity in vitro at concentrations less than 50 g/mL, but higher toxicity at higher concentrations such as 200 g/mL. At an HNT concentration of 200 g/mL, cell viability of mBMSCs and UMR-106 was 73.4% and 77.1% respectively. In vivo, HNTs inhibited *C. elegans* reproduction but had no effect on life spans or other phenotypes, indicating that HNTs did not have long-term toxicity effects. It indicated that HNTs have great biocompatibility at concentrations lower than 2.5 mg/mL. The toxicological investigations of these HNTs have a significant impact on their various biomedical uses.

4.1 Distribution and Translocation HNTs in Wild-Type Nematodes

Rhodamine B labeled HNTs was used to investigate whether and how HNTs are taken up by worms. The *C. elegans* were imaged after being incubated with these rhodamine-labeled nanoparticles from L1 larvae for 24 or 48 h. Representative nematodes with noticeable red fluorescence in the intestine were taken after 24 or 48 h of exposure. Furthermore, no HNT aggregation was found in *C. elegans* and the other tissue, including the uterus, vulva, and germline. These findings revealed that worms might ingest HNTs from the pharynx into the gut, as well as just uptaking nanomaterials without absorbing or digesting them.

HNTs are mostly taken up by *C. elegans* in the intestine, which is the major portion of the nematode responsible for metabolism. Factors affecting the metabolism of nematodes are the location of HNTs and their position in the gut. Oil-Red-O (ORO) staining was used to identify lipid metabolism. It was shown that wild-type animals treated with different concentrations of HNTs had no effect on ORO staining, suggesting that the distribution of HNTs in the intestine did not influence the metabolic activity in the intestine. Furthermore, the dye-leakage assay was used to examine the influence of HNTs on worm intestinal function. HNTs had no effect on dye leakage in animals, indicating that they did not affect the intestinal barrier function of *C. elegans.*

4.2 Toxic Effects of HNTs on the Reproduction and Growth of **C. elegans**

Changes in the phenotype of nematodes, such as reproduction, locomotion, or body length, are essential endpoints in toxicology. The effects of 1D nanoparticles on body length were investigated, and it was discovered that increasing the concentration of HNTs had no evident effect on body length. Furthermore, the body movement of rats treated with or without varying concentrations of HNTs was studied. Body movement is one of the most noticeable behavioral abnormalities associated with nematode aging. The research revealed that HNTs had no effect on *C. elegans* body movement. Because worms were known to produce offspring during the initial 5 days of adulthood, it was hypothesized that the early impacts of materials on nematode toxicity might be reflected in the influence of reproduction. The results showed that when animals were exposed to varying doses of HNTs, the total brood size of worms was dramatically reduced, but the hatching rate of worms was unaffected. The development of larvae is an important indicator for determining the toxicity of HNTs on larvae. These findings demonstrated that HNT exposure had no effect on worm growth. These results revealed that the adverse effects of HNTs on *C. elegans* are slightly, simply altering the brood size.

4.3 Toxic Effects of HNTs on the Life Span and ROS of **C. elegans**

The life span of an animal can reflect the long-term effects of some toxicants on it. It was found that exposure to HNTs had no effect on the lifetime of *C. elegans*, with the exception of worms exposed to 50 mg/mL, which showed a modest increase in life span (5.4%). These changes in lifetime may be related to decrease brood size, since several studies have found that an increase in life span usually accompanies a drop in progeny output. As a result, only *C. elegans* reproduction was affected by HNTs, but other characteristics like movement ability, body length, development, and longevity were little affected. It showed that HNTs did not have long-term toxicological effects. Despite their particle sizes (>100 nm), HNTs did not appear to be harmful.

In *C. elegans*, oxidative stress is typically a significant contributor to the toxicity caused by environmental toxins. The effects of HNTs in inducing ROS generation were further investigated. Using MitoSOX labeling, it was discovered that HNTs at varied concentrations did not clearly increase ROS formation; instead, mice exposed to 50 mg/mL exhibited moderately decreased ROS production. Furthermore, it was studied the influence of different HNT concentrations on the expression levels of genes associated with oxidative stress, including *sod-3*, *ctl-1* and *dod-3*. *sod-3*, a superoxide dismutase and *ctl-1*, a catalase, are crucial molecular bases for antioxidative stress response in *C. elegans*. *Dod-3*, a target gene of Forkhead box O transcription factor (FOXO) homolog DAF-16, is linked to oxidative stress. Expression of these oxidative stress-associated genes was hardly affected by HNTs, just dod-3 level was slightly elevated when animals were exposed to concentrations of 2.5, 10 and 50 mg/mL, and ctl-1 level was increased when worms were exposed to the concentration of 10 mg/mL. These findings revealed that when nematodes were exposed to HNTs, it might induce a light oxidative stress, which resulted in a small up-regulation of oxidation-related genes but did not result in a major increase in ROS generation.

5 Toxicity of Halloysite Toward Zebrafish

The zebrafish, which has 87% genetically homologous to human genes, is a tropical freshwater fish that is commonly used as a basic model organism for assessing toxicity in the environment. With its small scale and ease of observation, zebrafish embryos is a suitable model for studying the developmental toxicity of nanomaterials throughout the early life stage. For testing biomaterial nanotoxicity, zebrafish is often employed as a correlative and predictive model.

5.1 Acute Toxicity of HNTs in Zebrafish Embryos and Larvae

Systemic toxicity of HNTs was assessed using zebrafish embryos (AB wild type). [6]. HNTs (0.25, 0.5, 1, 2.5, 5, 10, 25, and 50 mg/mL) were investigated for acute toxicity to zebrafish embryos and larvae from 24 hpf to 120 hpf. HNTs (0.25, 0.5, 1, 2.5, 5, 10, 25, and 50 mg/mL) were investigated for acute toxicity to zebrafish embryos and larvae from 24 to 120 hpf. Zebrafish embryos and larvae exposed to various concentrations of HNTs cannot produce sufficient mortality to calculate LC_{50} values. Compared to the control group, the survival rate of zebrafish embryos and larvae does not change significantly at different developmental stages (24, 48, 72, 96, and 120 hpf) when treated with various concentrations of HNTs, whereas the high concentrations of HNTs (25 and 50 mg/mL) cause a significant survival decrease ($P < 0.01$). As time goes on, the survival of larvae emerges no obvious differences at each concentration of HNTs; Except for the maximum concentration of HNTs (50 mg/mL), there was a time response during the experiment and reached a level of the substantial difference in mortality (20%) at 72 hpf ($P < 0.001$). As a result, the findings suggest that HNTs have a limited influence on zebrafish survival. The morphology of zebrafish was studied between 72 to 120 hpf after exposing HNTs with different doses (0.25, 0.5, 1, 2.5, 5, 10, 25, and 50 mg/mL) in order to assess morphological deformity caused by HNTs. Except for the highest dose of HNTs (50 mg/mL) with a clear morphological deformity (10%), HNTs treated with varied concentrations show no significant difference from 72 to 120 hpf when compared to control groups. During developmental stages, the majority of larvae are in normal morphology. Many nanoparticles have been shown to cause developmental toxicity, including morphological deformity, such as S-doped TiO_2 nanoparticles, ZnO nanoparticles, and silica nanoparticles. Surprisingly, the actions of HNTs are different from those of the previously stated nanoparticles. Our findings show that HNTs at varying dosages (25 mg/mL) have no effect on zebrafish morphological development.

5.2 *Sublethal Effects of HNTs on the Development of Zebrafish*

Hatchability between 48 and 72 hpf is regarded as a pivotal period for zebrafish's chorion hatchability and embryo genesis. The relationship between successful embryo genesis and embryo toxicity is a critical measure for assessing nanotoxicity. Hatchability was measured at 48, 54, 60, 66, and 72 hpf to determine if varying concentrations of HNTs had a potentially harmful effect on embryo hatching delay. Hatching necessitates the production of proteolytic enzymes from the hatching gland to soften the chorion and larval movement to break free; various xenobiotics have been reported to prevent this step. So far, various nanomaterials have been highlighted as existing hatching delays and harmful effects on zebrafish development. For instance, GO or multi-walled CNTs (50 mg/L) may cause embryo hatching delays due to changes in chorion flexibility and chorionic hatching enzyme function. However, HNTs considerably improve the hatchability of zebrafish embryos in various degrees from 48 to 72 hpf in comparison with the control group, with only the highest dose (50 mg/mL) of HNTs showing a lagging hatchability. When combined with the studies of the acute toxicity of HNTs in zebrafish embryos and larvae, it is shown that zebrafish embryos exposed to HNTs at a concentration of 50 mg/mL exhibit a low survival rate, a delay in hatching, and a high malformation rate. In other words, exposing zebrafish embryos to HNTs ($\leq$25 mg/mL) can induce hatching without malformation and with a high survival rate. The enhancing hatching rate of zebrafish embryos induced by HNTs may be contributed to the needle-like fiber shape of HNTs which can penetrate the cell membrane easily. This confirms that HNTs are safe for zebrafish embryos at a dose of $\leq$25 mg/mL.

During the 17–30 hpf developmental window, zebrafish embryos demonstrate spontaneous movement (coiling and flexing). A basic and practical way to monitor zebrafish behavior is to view larvae directly under a microscope and count spontaneous movement during specific period. At 24, 48, 72, 96, and 120 hpf, spontaneous movement in 20 s of zebrafish exposed to HNTs (0, 0.25, 2.5, 5, 25, and 50 mg/mL) at 6 hpf was recorded. At 24, 48, 72, and 96 hpf, all zebrafish with varied doses exhibit no significant alterations in spontaneous movement. Just spontaneous movement of zebrafish larvae at 120 hpf shows a significant dose-dependent relationship. The highest number of spontaneous movements was in the control group of zebrafish. Additionally, when the concentration of HNTs increases, the spontaneous movement periods of zebrafish larvae decrease. For instance, zebrafish larvae in the 50 mg/mL, 2.5 mg/mL, and 0.25 mg/mL HNTs-treated groups moved 8, 10, and 12 times, respectively, while moved 17 times in 20 s in the control group. As a result, it is possible to conclude that HNTs existing in zebrafish living environments have little effect on zebrafish behavior, such as spontaneous movements.

The heart rate of zebrafish was counted in 10 s and recorded at 24, 48, 72, 96, and 120 hpf to assess cardiac toxicity following treatment with HNTs (0, 0.25, 2.5, 5, 25, and 50 mg/mL). When zebrafish are exposed to varied doses of HNTs from 24 to 120 hpf, there are no noticeable changes in heart rate, demonstrating that HNTs cannot cause cardiac toxicity throughout zebrafish development.

5.3 Distribution of HNTs in Zebrafish Embryos and Larvae

Because HNTs have no influence on acute or sublethal toxicity in zebrafish development, it is uncertain if HNTs might be digested by the zebrafish or enriched on the surface of the chorion. The enrichment of HNTs on the surface of the chorionic membrane of zebrafish embryos can be observed by fluorescence microscopy, scanning electron microscopy and light microscopy. Moreover, FITC-HNTs are designed to allow clear observation of this behavior using a fluorescence microscope. HNTs are dose-dependently enriched on the chorion surface of embryos. When the concentration of HNTs is more than 25 mg/mL, the zebrafish embryos are completely encircled by the nanotubes. The embryos were discovered to have FITC-HNT coverage because they exhibit enhanced green fluorescence with increasing FITC-HNT concentrations. However, it is unclear if HNTs can accumulate inside embryos. Previous studies have found that the chorionic membrane of zebrafish embryos act as a protective barrier for the agglomerates, as SWCNTs agglomerates can adhere to the chorionic membrane surface of the embryo but cannot pass through the pores in the embryo because the size of the agglomerates is too large. The enrichment of HNTs on the surface of the chorion is comparable to that of SWCNTs. As a result, aggregates of HNTs may not be swallowed by zebrafish embryos.

Under a fluorescent microscope, zebrafish larvae were observed the ingestion of HNTs. The fluorescence of FITC-HNTs (25 mg/mL) without larvae is shown as a blank group to demonstrate that the fluorescence of FITC-HNTs cannot naturally diminish during the experiment. It has been discovered that varied doses (0.25, 2.5, and 25 mg/mL) of FITC-HNTs may be ingested by zebrafish larvae and mostly concentrate in the gastrointestinal system. The fluorescence intensity of FITC-HNTs ingested by zebrafish larvae steadily declines over time, indicating that FITC-HNTs can be expelled by zebrafish larvae via gastrointestinal metabolism. The findings show that HNTs can be excreted by zebrafish larvae. Overall, HNTs ($\leq$ 25 mg/mL) may enrich on the surface of the chorion, be eaten, and excreted by zebrafish larvae with no notable harmful consequences during the zebrafish development period. HNTs are hazardous to mice according to new research. HNTs can be ingested by the intestinal epithelium of mice and cause harmful effects on the animals' liver and lungs via intragastric feeding. The harmful effects of HNTs vary due to differences in animal models. Throughout this study, HNTs are dispersed in the zebrafish living environment and absorbed by zebrafish larvae. Previous research has demonstrated that nanoparticles may be absorbed by the intestinal epithelium and then expelled by zebrafish larvae. In zebrafish, egg water stimulates body fluid circulation, reducing toxicity to other main organs. Overall, it can be concluded that HNTs are biocompatible nanomaterials.

6 Conclusion

In this review, we summarized the toxicity research progress of HNTs using different models. Due to the unique morphology of HNTs and developed industrial application, the environmental safety of HNTs became a hot topic in the clay area. The current data shows that the toxicity of HNTs is very low and can be tailored by changing the dose. They are safe to crop growth and alga living as well as fish and nematodes. More experiment data on the big animal models should be acquired before HNTs are used in products contacting the human body. Also, blood compatibility and tumorigenic should be assessed for a long period time. Respiratory intake should be strictly prohibited since the tubes can damage the lung.

References

1. Liu, M., Jia, Z., Jia, D., Zhou, C.: Recent advance in research on halloysite nanotubes-polymer nanocomposite. Prog. Polym. Sci. **39**, 1498–1525 (2014)
2. Zhao, X., Zhou, C., Liu, M.: Self-assembled structures of halloysite nanotubes: towards the development of high-performance biomedical materials. J. Mater. Chem. B **8**, 838–851 (2020)
3. Chen, L., Guo, Z., Lao, B., Li, C., Zhu, J., Yu, R., et al.: Phytotoxicity of halloysite nanotubes using wheat as a model: seed germination and growth. Environ. Sci. Nano **8**, 3015–3027 (2021)
4. Huang, X., Huang, Y., Wang, D., Liu, M., Li, J., Chen, D.: Cellular response of freshwater algae to halloysite nanotubes: alteration of oxidative stress and membrane function. Environ. Sci. Nano **8**, 3262–3272 (2021)
5. Zhao, X., Wan, Q., Fu, X., Meng, X., Ou, X., Zhong, R., et al.: Toxicity evaluation of one-dimensional nanoparticles using *Caenorhabditis elegans*: a comparative study of halloysite nanotubes and chitin nanocrystals. ACS Sustain. Chem. Eng. **7**, 18965–18975 (2019)
6. Long, Z., Wu, Y.-P., Gao, H.-Y., Zhang, J., Ou, X., He, R.-R., et al.: In vitro and in vivo toxicity evaluation of halloysite nanotubes. J. Mater. Chem. B **6**, 7204–7216 (2018)

Index

M. Vithanage et al. (eds.), *Clay Composites*, Advances in Material Research and Technology, https://doi.org/10.1007/978-981-99-2544-5