Maulin Shah
Aditi Banerjee *Editors*

Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant

Springer

Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant

Maulin Shah • Aditi Banerjee
Editors

Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant

Springer

Editors
Maulin Shah
Industrial Waste Water Research Lab,
Division of Applied & Environmental
Microbiology
Enviro Technology Limited
Ankleshwar, Gujarat, India

Aditi Banerjee
Centre for Nano Technology
Indian Institute of Technology-Guwahati
Guwahati, Assam, India

ISBN 978-981-15-0496-9 ISBN 978-981-15-0497-6 (eBook)
https://doi.org/10.1007/978-981-15-0497-6

© Springer Nature Singapore Pte Ltd. 2020
This work is subject to copyright. All rights are reserved 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

With the ever-growing urbanization, industrial progress, and overall development, natural resources are being affected by pollutants and contaminants, which are causing harmful and toxic effects on natural flora and fauna. In this regard, recycling and remediation seem the need of the hour. However, the approach can only be implemented properly with comprehensive knowledge of the available technologies and their expanding nature of application. For sustainable and futuristic development, the industries must integrate the best remediation process in their plans. Chemicals discharged from industries cover the air, water, and soil; and no singular approach or method can deal with the aftermath they cause. Toxic pollutants can be divided into two broad categories: inorganic and organic. Using existent technologies and processes, the development of state-of-the-art and cost-effective solution to address the ground-level problem is the main challenge. In this context, grouping the physical and chemical applications with existent conventional biological treatment enhances the results in shorter time.

Excessive pollutants in water and soil affect the nutrition level in crops and food and pose serious threat to health. Availability of fresh drinking water is scarce today. To be treated efficiently by bioremediation process, pollutants have to be biologically accessible and enzymatically breakable by microorganism. Favorable environmental conditions make the breakdown faster. But, like all other technologies, bioremediation too has its limitation, i.e., recalcitrant molecules. There, the evolution of recycle and remediation method has enabled to use a combination of different and complex technologies and bring them together for better outcome and faster process. Keeping the urgency of application in mind, bioremediation became the integral part of research, academia, government policies, and industrial planning. With improved, practical, and stricter policies, effective development and multidisciplinary research approach are being encouraged for economical remediation process. With every trial, researchers are trying to build more imperative green economical and efficient treatment process for the application. This book elaborately discussed the waste treatment methods and techniques for water and soil conservation, in aerobic or anaerobic ways, with or without microorganism, with practicality and efficiency.

This book will be useful and applicable for the skilled as well as the beginners in this field. The chapters discuss contemporary techniques and technologies, with elaborate methodologies along with their advantages and disadvantages, which make the book globally relevant.

Ankleshwar, India — Maulin Shah
Guwahati, India — Aditi Banerjee

Contents

About the Editors

Maulin P. Shah is Chief Scientist & Head of the Industrial Waste Water Research Lab, Division of Applied and Environmental Microbiology Lab at Enviro Technology Ltd., Ankleshwar, Gujarat, India. His work focuses on the impact of industrial pollution on the microbial diversity of wastewater, and genetically engineering high-impact microbes for the degradation of hazardous materials. He is an active editorial board member in top-rated journals.

Dr. Aditi Banerjee currently holds an Independent Research Scientist position in the Centre for Nanotechnology, IIT Guwahati, supported by the Department of Science and Technology, Government of India. She started her research career as an environmentalist, focusing on treating petrochemical and refinery generated wastewater by biological methods. She has long expertise in designing and solving environmental-related issues concerning soil, water, and air. Her wide experience transcends into interdisciplinary approaches and application of treating and making wealth from waste. She has published more than 15 international research publications and 2 books.

By-Products from Forest Activities as Low-Cost Sorbents for Bioremediation of Effluents and Other Polluted Media

1

Avelino Núñez-Delgado, Esperanza Álvarez-Rodríguez,
María J. Fernández-Sanjurjo, Manuel Arias-Estévez,
Juan Carlos Nóvoa-Muñoz, David Fernández-Calviño,
and Manuel Conde-Cid

Abstract

In this chapter, we review available data on the use of forest waste and by-products to remove pollutants. We focus on by-products from forest industry due to their proved efficacy for some specific contaminants and also due to the economic and social relevance of forest industry, as well as to the overall repercussion of recycling these waste materials when considering carbon storage and cycling at local and global scales. The treatment of both water and soil pollution is covered, also differencing among individual wastes and among specific pollutants, due to the various responses found regarding pollution removal and/or retention for different contaminants by using each by-product and on each environmental compartment.

Keywords
Bio-sorbents · Forest waste · Remediation · Soil pollution · Water pollution

1.1 Introduction

Waste materials and many by-products have been a matter of concern, and recycling them correctly is still a task deserving great efforts. However, they are also increasingly viewed as an economic (or business) opportunity, implying a need of surveillance and care to give real priority to people and the overall environment

---

A. Núñez-Delgado (✉) · E. Álvarez-Rodríguez · M. J. Fernández-Sanjurjo
Department of Soil Science and Agricultural Chemistry, Engineering Polytechnic School, University of Santiago de Compostela, Lugo, Spain
e-mail: avelino.nunez@usc.es

M. Arias-Estévez · J. C. Nóvoa-Muñoz · D. Fernández-Calviño · M. Conde-Cid
Soil Science and Agricultural Chemistry, Faculty of Sciences, University of Vigo, Ourense, Spain

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_1

(Núñez-Delgado 2014, 2015a, b, c). From a technical point of view, it has been shown that it is clearly interesting and promising to recycle both raw and modified waste and by-products (Núñez-Delgado et al. 2015a). And among them, those derived from forest activities can be considered of special relevance, mainly in countries where forest industries are of main importance, as is the case of Galicia (NW Spain) and many other geographic areas and countries around the world.

1.2 Data on the Use of Forest Waste and By-Products as Sorbents in Bioremediation

1.2.1 The Situation in Galicia (NW Spain)

Some forest by-products, as wood ash, have been used to facilitate decontamination of sewage sludge and other waste. In certain cases, it was based on appropriate sludge/ash technical mixing (Pousada-Ferradás et al. 2012), thus increasing sorption and decreasing risks linked to leaching of pollutants. Photograph 1.1 shows original (not previously published) scanning electron microscopy (SEM) images of wood ash included in those waste mixtures.

In other cases, sludge and wood ash were combined with other various waste materials, such as mussel shell calcination ash (Seco-Reigosa et al., 2014), giving final mixtures with strong As and Hg retention potential and also reducing risks of soil and water pollution (see Photograph 1.2 for original SEM images of some of these mixtures).

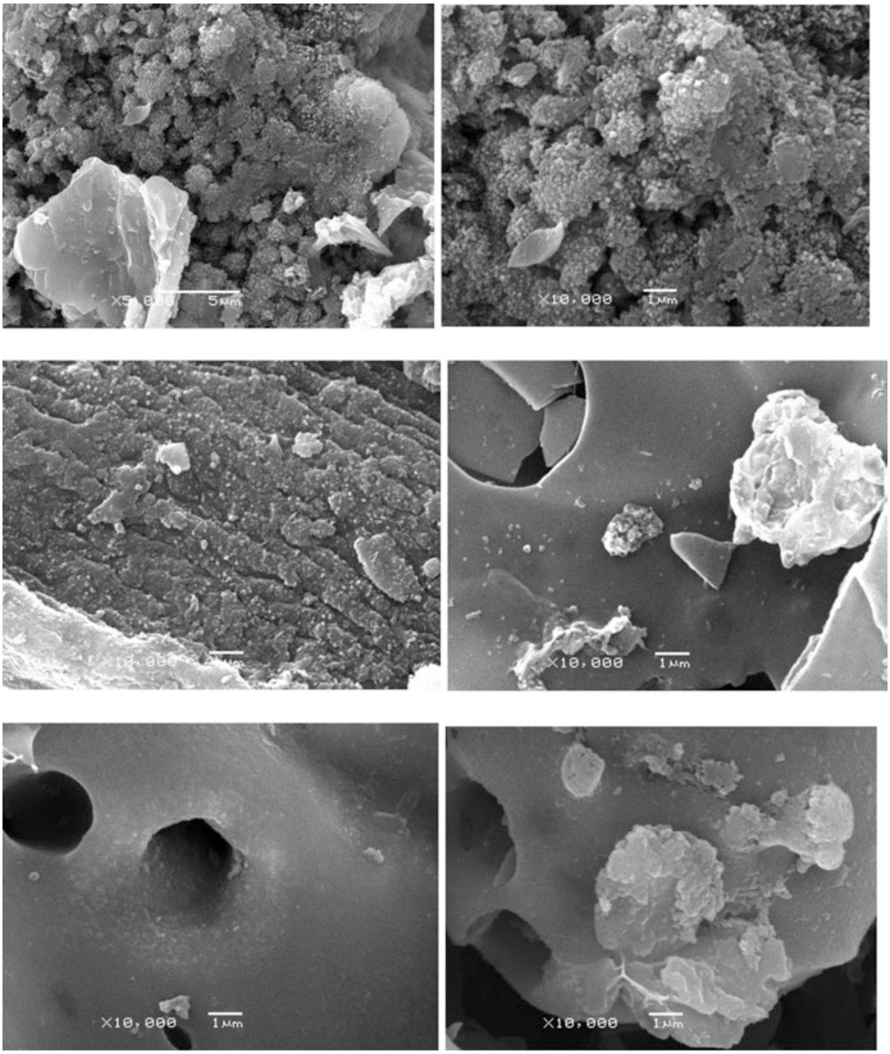
Other treatment alternatives were performed to reach inactivation/retention of abiotic and biotic contaminants through composting, this time including vegetable remains together with sewage sludge and wood ash (Estévez-Schwarz et al. 2009, 2012) (see Photograph 1.3).

Various kinds of forest by-products have been studied to remove different contaminants from polluted media. Photographs 1.4 and 1.5 are original not amplified and SEM images (not previously published) showing two examples of these by-products (pine bark and oak wood ash).

A synthesis of the main results regarding sorption/desorption efficacy is presented in Table 1.1.

Specifically, Seco-Reigosa et al. (2013) found As(V) adsorption higher than 97%, with desorption <1%, using pine wood ash, while lower efficacy was reported for oak wood ash, and it was clearly lower for pine sawdust. Quintáns-Fondo et al. (2017) reported As(V) sorption >87% and <7% desorption for oak ash, while pine bark sorbed <3% and desorbed 100%.

Núñez-Delgado et al. (2015b) studied Cr(VI) retention on pine sawdust and oak wood ash, finding poor results for both materials (sorption 23% and 17%, respectively). Rivas-Pérez et al. (2017) found sorption up to 50% higher for As(V) than for Cr(VI) on oak ash, whereas it was 95% higher for Cr(VI) on pine bark. Regarding the effects of amendments on soil samples, oak ash increased As(V) retention, pine bark increased Cr(VI) sorption, and, in addition, pine bark amendment increased Cr(VI) sorption on pyritic material.

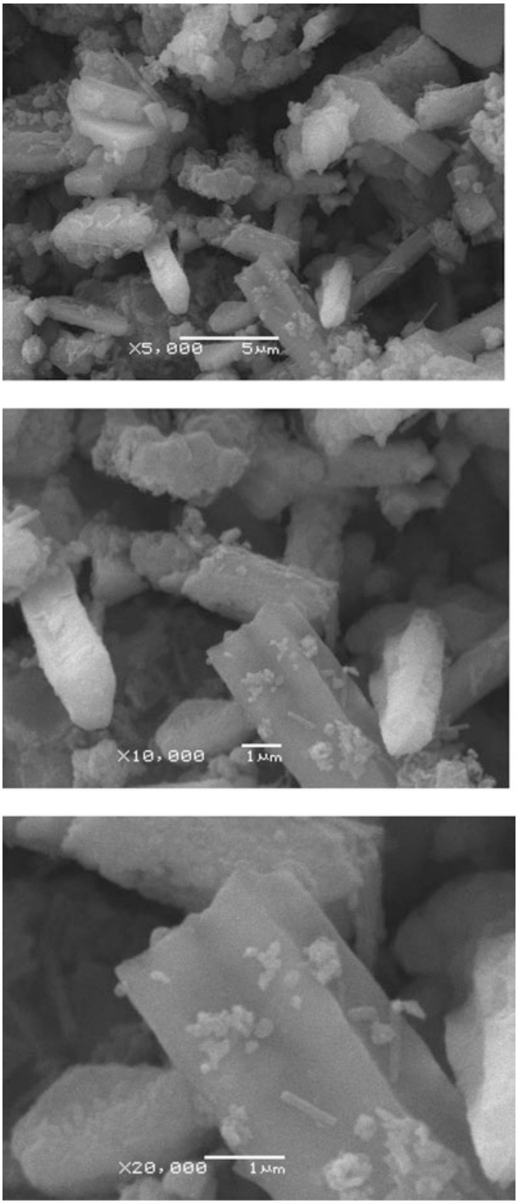


Photograph 1.1 SEM images of wood ash. (Original from authors, not previously published)

Quintáns-Fondo et al. (2016b) studied As(V)/Cr(VI) competitive sorption on pine bark and oak ash, finding more affinity for As(V) sorption in oak ash (sorption up to >84 %), whereas Cr(VI) sorption was clearly higher in pine bark (>90 %). They also found that oak ash could be used to remove high concentrations of As(V), even in the presence of a wide range of Cr(VI) contents, while pine bark could be used to remove high Cr(VI) concentrations.

Romar-Gasalla et al. (2016) studied P retention on pine sawdust and on a mixture including sewage sludge, mussel shell ash, and pine wood ash, with P sorption reaching only around 40% for pine sawdust, whereas clearly better results were

Photograph 1.2 SEM images of waste mixtures including wood ash. (Original from authors, not previously published)



reported for the mixture (70–90% retention). Romar-Gasalla et al. (2018a) found that initial poor P retention on pine sawdust improved with prolonged contact time.

Rivas-Pérez et al. (2015) studied As(V) and P competitive sorption on pine sawdust, and they reported clearly higher affinity for P.

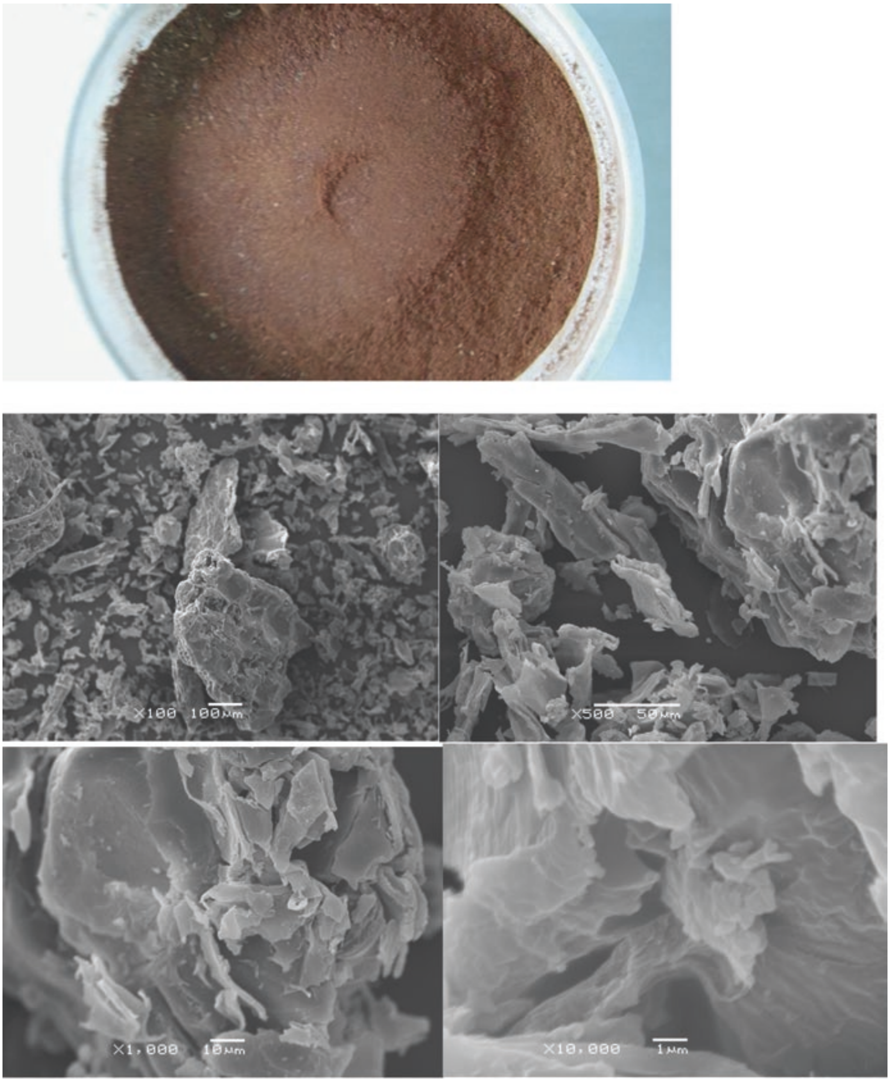
Photograph 1.3 Piles during composting at pilot scale. (Original from authors, not previously published)

Quintáns-Fondo et al. (2016a) studied different forest waste and by-products; one of them was a waste mixture including pine wood ash, which showed >73% sorption capacity for F^-, with poorer results for wood ash alone and for pine sawdust. Quintáns-Fondo et al. (2018) found high F^- sorption on oak wood ash, even at alkaline pH (it was close to 100% at pH < 6, and around 70% at pH 10), while F^- sorption was low on pine sawdust, at any pH. They also reported that competition for sorption sites between As(V) and F^- was almost negligible.

Romar-Gasalla et al. (2018b) found that for pine bark, Cr(VI) sorption was > 97% and desorption <1.5%, while for oak ash, Cr(VI) sorption was < 32%. Regarding F^- retention, sorption was 62–73% and desorption 10–15% in pine bark, whereas in oak ash, sorption was 60–69% and desorption 11–14%. When added to forest and vineyard soils and to pyritic material, both by-products increased F^- sorption and decreased desorption, while pine bark increased Cr(VI) retention on both soils and pyritic material.

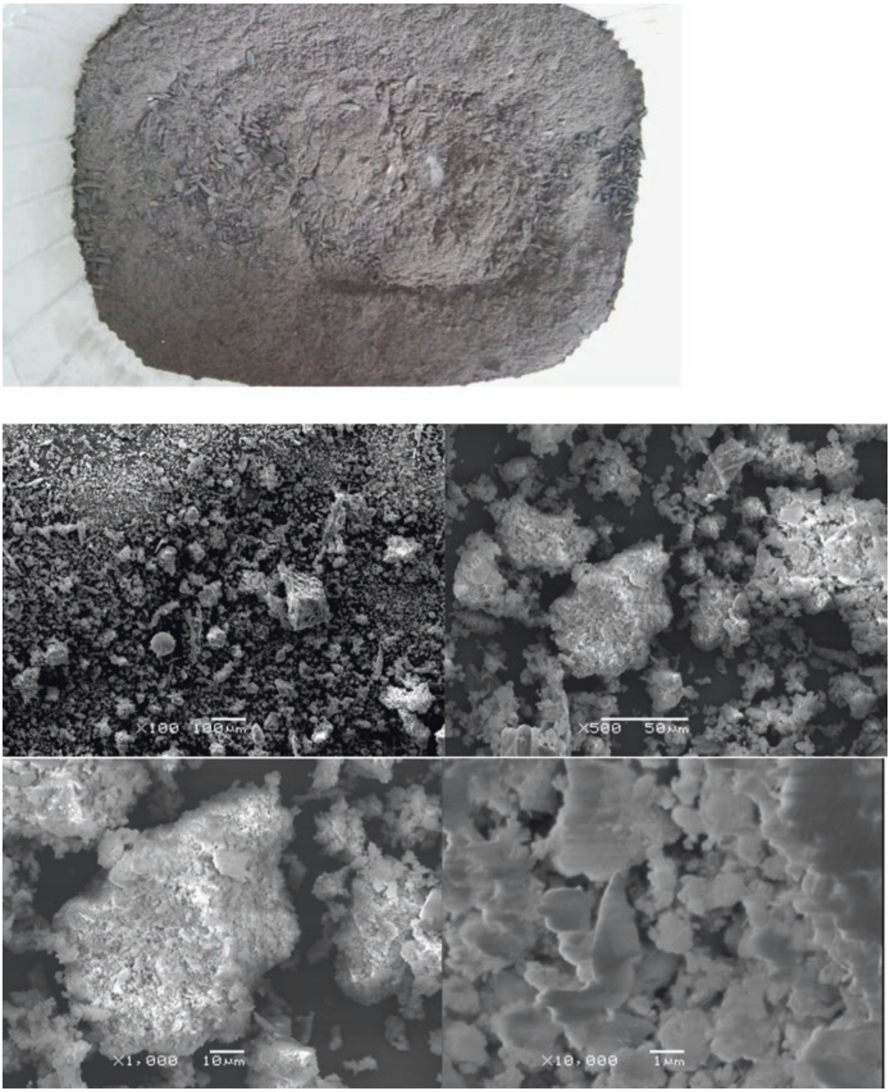
Núñez-Delgado et al. (2017) found that oak ash amendment clearly increased Cd and Pb sorption on soils and pyritic material (reaching near 100%) and decreased desorption, while results were rather low for pine bark amendment.

As regards works that focused specifically on pine bark, Cutillas-Barreiro et al. (2014) found that adsorption was between 98 and 99% for Pb, 83–84% for Cu, 78–84% for Cd, 77–83% for Zn, and 70–75% for Ni, with those differences being



Photograph 1.4 Pine bark: not amplified image and SEM images. (Original from authors, not previously published)

mainly due to different affinity for adsorption sites. In another work, Paradelo et al. (2016) studied the potential of pine bark as adsorbent when heavy metals circulated through it into laboratory columns, finding 100% removal for low metal concentrations (2.5 mM), whereas just 16–43% was retained when the highest metal concentration (25 mM) was assayed. These authors reported a progressive adsorption of the metals entering the column, followed by a significant release when a saturation concentration is reached. Cutillas-Barreiro et al. (2016) studied



Photograph 1.5 Oak wood ash: not amplified image and SEM images. (Original from authors, not previously published)

competitive sorption/desorption for heavy metals in pine bark, with results showing retention in the order Pb>Cu>Zn>Cd>Ni, as well as a strong influence of Pb and Cu on the retention of the other metals. In another work, Cutillas-Barreiro et al. (2017) studied the efficacy of pine bark to control Cu pollution in acid vineyard soils. These authors found that pine bark amendment decreased Cu levels in shoots and roots of grass growing in that environment, mostly due to a significant decrease in the most mobile Cu fractions in the soil. Fernández-Calviño et al. (2017) studied the effects

Table 1.1 Sorption (and desorption) percentages for different pollutants achieved by various authors in Galicia (Spain) using different forest waste and by-products as sorbent materials

Sorbent	Pollutant	% Sorp. (desorp.)	Country	Source
Pine wood ash	As(V)	>97 (<1)	Galicia (Spain)	Seco-Reigosa et al. (2013)
Oak wood ash	As(V)	67–80 (6–8)	Galicia (Spain)	Seco-Reigosa et al. (2013)
Oak wood ash	As(V)	>87 (<7)	Galicia (Spain)	Quintáns-Fondo et al. (2017)
Oak wood ash	Cr(VI)	17	Galicia (Spain)	Núñez-Delgado et al. (2015b)
Oak wood ash	As(V)	>84	Galicia (Spain)	Quintáns-Fondo et al. (2016b)
Oak wood ash	As(V)	91–95	Galicia (Spain)	Rivas-Pérez et al. (2017)
Oak wood ash	Cr(VI)	37–60	Galicia (Spain)	Rivas-Pérez et al. (2017)
Oak wood ash	Cr(VI)	<32	Galicia (Spain)	Romar-Gasalla et al. (2018b)
Oak wood ash	F^-	70–99	Galicia (Spain)	Quintáns-Fondo et al. (2018)
Oak wood ash	F^-	60–69 (11–14)	Galicia (Spain)	Romar-Gasalla et al. (2018b)
Pine sawdust	As(V)	43–60 (32–50)	Galicia (Spain)	Seco-Reigosa et al. (2013)
Pine sawdust	Cr(VI)	23	Galicia (Spain)	Núñez-Delgado et al. (2015b)
Pine sawdust	P	40	Galicia (Spain)	Romar-Gasalla et al. (2016)
Pine bark	Pb	98–99	Galicia (Spain)	Cutillas-Barreiro et al. (2014)
Pine bark	Cu	83–84	Galicia (Spain)	Cutillas-Barreiro et al. (2014)
Pine bark	Cd	78–84	Galicia (Spain)	Cutillas-Barreiro et al. (2014)
Pine bark	Zn	77–83	Galicia (Spain)	Cutillas-Barreiro et al. (2014)
Pine bark	Ni	70–75	Galicia (Spain)	Cutillas-Barreiro et al. (2014)
Pine bark	Cr(VI)	>90	Galicia (Spain)	Quintáns-Fondo et al. (2016b)
Pine bark	As(V)	<3 (100)	Galicia (Spain)	Quintáns-Fondo et al. (2017)
Pine bark	Cr(VI)	95–96	Galicia (Spain)	Rivas-Pérez et al. (2017)
Pine bark	Cr(VI)	> 97 (<1.5)	Galicia (Spain)	Romar-Gasalla et al. (2018b)

(continued)

Table 1.1 (continued)

Sorbent	Pollutant	% Sorp. (desorp.)	Country	Source
Pine bark	F^-	62–73 (10–15)	Galicia (Spain)	Romar-Gasalla et al. (2018b)
Pine bark	Cr(VI)	99	Galicia (Spain)	Paradelo et al. (2017)
Waste mixture	P	70–90	Galicia (Spain)	Romar-Gasalla et al. (2016)
Waste mixture	F^-	>73	Galicia (Spain)	Quintáns-Fondo et al. (2016a)

of both pine bark amendment and ageing in mine soils, finding a decrease in the soluble fractions and an increase in less mobile fractions for Cu and Pb, as well as a decrease in metal release. Paradelo et al. (2017) showed that pine bark has very high retention potential for dichromate (sorption close to 100% and less than 2% desorption), but very low retention capacity for phosphate, arsenate, or fluoride, with different mechanisms governing sorption of the various anionic pollutants. Fernández-Calviño et al. (2018) studied the effect on microbial function due to pine bark amendment on Cu-polluted mine soils, finding that pine bark increased fungal growth throughout the 2-year period of the study. In addition, the use of 1:1 pine-bark/mussel-shell mixtures favored growth for both bacteria and fungi.

1.2.2 Overall Situation on a Global Basis and Future Perspectives

Considering data from different countries around the world, just 26 results were provided when searching for “Forest by-products AND Remediation” on Web of Science (WOS) (Clarivate Analytics), while searching for “Forest Waste AND Remediation,” the number of results was 790. For the latter, WOS tools show that 37–53 papers were published yearly, considering from year 2010 to 2015, then reaching a maximum of 98 papers during 2016, decreasing to 95 in 2017, and to 66 in 2018. By the end of March 2019, 5 new papers were published on the matter. Regarding countries, 141 papers were from the USA, 95 from China, 58 from Spain, 57 from India, 41 from Italy, 40 from Canada, 40 from Germany, 38 from Australia, 34 from Brazil, and 32 from Poland.

However, when searching for “Forest Waste AND Remediation” on Google Scholar (GS), a higher score of 66,400 results was provided. Even when searching for “Forest by-products AND Remediation” on GS, the number of results was 9810, clearly higher than that from WOS. To view this last number in more detail, 25 results were found till 1980, 90 results between 1981 and 1990, 700 results between 1991 and 2000, 1010 results between 2001 and 2005, and 1360 results between 2006 and 2009. Considering the same years as in the report from WOS, GS found 433 results in 2010, 500 results in 2011, 551 in 2012, 612 in 2013, 689 in 2014, 720 in 2015, 796 in 2016, 806 in 2017, 815 in 2018, and 212 in 2019 (till the end of March), which means that, contrary to WOS, GS did not find a decreasing trend for any interval or specific year.

In previous reviews, Chen et al. (2011) reported a great potential for plant residues (including forest waste) for polycyclic aromatic hydrocarbon removal from wastewater. In a more general manner, these authors commented that raw and modified plant residues are a promising choice for organic pollutant treatment due to their low cost, environmental compatibility, high sorption capability, and ubiquity in the environment.

Saka et al. (2012) indicated that the use of forest (and agricultural) waste adsorbents to remove heavy metals (and specifically Pb^{2+}) from wastewaters has clearly grown, mainly due to the fact of being inexpensive, biodegradable, abundant, and efficient, making them very attractive compared to activated carbon.

Bilal et al. (2013) indicated that forest (and agriculture) waste bio-adsorbents showed high potential for Cu removal, which was due to remarkable adsorption capacities, low cost, and availability, as well as to their mono- to multilayer adsorption behavior. These authors found the following Cu adsorption sequence for different bio-sorbents (including forest by-products): activated carbon > algal > bacterial > agriculture and forest > fungal > yeast biomass. Regarding mechanisms, Bilal et al. (2013) commented that ion exchange and complexation are the two most important processes affecting metal uptake by bio-adsorbents. Finally, they indicated that the major challenges for bio-adsorption are appropriate reuse and chemical modifications of bio-adsorbents.

In a review paper dealing with plant-based biomass (including forest waste), Jain et al. (2016) indicated that these materials remove efficiently diverse toxic metals from water/wastewater. These authors also indicate the need of pilot studies at industrial scale, as well as the development of efficient and economical bio-sorbents for wastewater treatment with commercial level properties.

Focusing on reutilization of sorbents, Reddy et al. (2017) indicated that emerging post-sorption technologies are allowing adsorption products to subsequently be used as fertilizers, in catalysis, in carbonaceous metal nanoparticle synthesis, as feed additives, and as biologically active compounds.

Pyrzynska (2019) reviewed the use of low-cost adsorbents (including forest waste) for Cd removal. This author indicated that although modified bio-sorbents showed better adsorption capacities than those unmodified, these procedures increased cost, reducing their advantages compared to conventional adsorbents and also raising serious environmental questions on eventual generation of toxic wastes. The author indicated that comparing techno-economically low-cost adsorbents and activated carbon, higher effectiveness was found for green low-cost materials, taking into account cost of synthesis and regeneration. Pyrzynska (2019) also commented on the lack of results at pilot plant scale, which should be solved to promote large-scale use of these low-cost adsorbents.

1.3 Conclusions and Future Trends

In this book chapter, we reviewed works carried out in Galicia (NW Spain) regarding the use of forest waste and by-products to remove contaminants from polluted solid and liquid environments, notably soil and water. Most works focused on heavy metals/metalloids, while others dealt with P and F^-. This chapter put together data from a number of papers, considering both sorbents and pollutants, showing which sorbents are effective (and in which extent) for the removal of different contaminants. Considering the matter globally, searching tools for academic and research works find a huge amount of results, and these tools show differing results. In one case, the conclusion would be that the number of research papers is decreasing since 2016, while another tool shows a continued progressive increase. In any case, it is clear that the scientific community and the society as a whole are concerned about effective recycling of forest waste, and most actors agree on the convenience of promoting research and use of raw (or in certain cases modified) forest by-products to fight environmental pollution affecting soil and water bodies. Recently, an increasing interest is focusing on the efficient reuse of already utilized sorbents, which also deserves more future research.

As regards contaminants to be treated, the authors of this chapter consider that forest by-products could be very interesting as active materials for the retention/removal of antibiotics and other emerging pollutants from waters, sewage sludge, or soils receiving the spreading of polluted waters and/or sludge.

Acknowledgments Funding: This work was supported by the Spanish Ministry of Economy and Competitiveness [grant numbers CGL2015-67333-C2-1-R and CGL2015-67333-C2-2-R]. It also received funds from the European Regional Development Fund (ERDF) (FEDER in Spain), being a complement to the previous grants, without additional grant number. D. Fernández-Calviño holds a Ramón y Cajal contract (RYC-2016-20411) financed by the Spanish Ministry of Economy, Industry and Competitiveness. M. Conde-Cid holds a pre-doctoral contract (FPU15/0280, Spanish Government). The sponsors had no involvement in the study design; in the collection, analysis, and interpretation of data; in the writing of the report, and in the decision to submit the article for publication.

References

Bilal M, Shah JA, Ashfaq T, Gardazi SMH, Tahir AA, Pervez A, Haroon H, Mahmood Q (2013) Waste biomass adsorbents for copper removal from industrial wastewater—a review. J Hazard Mater 263(2):322–333. https://doi.org/10.1016/j.jhazmat.2013.07.071

Chen B, Yuan M, Liu H (2011) Removal of polycyclic aromatic hydrocarbons from aqueous solution using plant residue materials as a biosorbent. J Hazard Mater 188(1–3):436–442. https://doi.org/10.1016/j.jhazmat.2011.01.114

Cutillas-Barreiro L, Ansias-Manso L, Fernández-Calviño D, Arias-Estévez M, Nóvoa-Muñoz JC, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Núñez-Delgado A (2014) Pine bark as bio-adsorbent for Cd, Cu, Ni, Pb and Zn: batch-type and stirred flow chamber experiments. J Environ Manag 144:258–264. https://doi.org/10.1016/j.jenvman.2014.06.008

Cutillas-Barreiro L, Paradelo R, Igrexas-Soto A, Núñez-Delgado A, Fernández-Sanjurjo MJ, Álvarez-Rodriguez E, Garrote G, Nóvoa-Muñoz JC, Arias-Estévez M (2016) Valorization of biosorbent obtained from a forestry waste: competitive adsorption, desorption and transport of Cd, Cu, Ni, Pb and Zn. Ecotoxicol Environ Saf 131:118–126. https://doi.org/10.1016/j.ecoenv.2016.05.007

Cutillas-Barreiro L, Fernández-Calviño D, Núñez-Delgado A, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Nóvoa-Muñoz JC, Arias-Estévez M (2017) Pine bark amendment to promote sustainability in Cu-polluted acid soils: effects on *Lolium perenne* growth and Cu uptake. Water Air Soil Pollut 228:260. https://doi.org/10.1007/s11270-017-3437-y

Estévez-Schwarz I, Seoane S, Núñez A, López-Mosquera ME (2009) Characterization and evaluation of compost utilized as ornamental plant substrate. Compost Sci Util 17(4):210–219. https://doi.org/10.1080/1065657X.2009.10702426

Estévez-Schwarz I, Seoane S, Núñez-Delgado A, López-Mosquera ME (2012) Production and characterization of compost made from garden and other waste. Pol J Environ Stud 21(4):855–864

Fernández-Calviño D, Cutillas-Barreiro L, Paradelo-Núñez R, Nóvoa-Muñoz JC, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Núñez-Delgado A, Arias-Estévez M (2017) Heavy metals fractionation and desorption in pine bark amended mine soils. J Environ Manag 192:79–88. https://doi.org/10.1016/j.jenvman.2017.01.042

Fernández-Calviño D, Cutillas-Barreiro L, Nóvoa-Muñoz JC, Díaz-Raviña M, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Núñez-Delgado A, Arias-Estévez M, Rousk J (2018) Using pine bark and mussel shell amendments to reclaim microbial functions in a Cu polluted acid mine soil. Appl Soil Ecol 127:102–111. https://doi.org/10.1016/j.apsoil.2018.03.010

Jain CK, Malik DS, Yadav AK (2016) Applicability of plant based biosorbents in the removal of heavy metals: a review. Environ Process 3(2):495–523. https://doi.org/10.1007/s40710-016-0143-5

Núñez-Delgado A (2014) Waste or gold? J Clean Prod 83:497. https://doi.org/10.1016/j.jclepro.2014.07.014

Núñez-Delgado A (2015a) Take the waste and run (Correspondence on: Riding MJ, Herbert BMJ, Ricketts L, Dodd I, Ostle N, Semple KT (2015) Harmonising conflicts between science, regulation, perception and environmental impact: the case of soil conditioners from bioenergy. Environ Int 75:52–67). Environ Int 77, 161. https://doi.org/10.1016/j.envint.2015.01.015

Núñez-Delgado A (2015b) Welfare index, waste and expropriation. J Clean Prod 96:10–11. https://doi.org/10.1016/j.jclepro.2015.01.092

Núñez-Delgado A (2015c) Scientists talking to politicians: could you please save the environment? (Correspondence on Diamond et al. (2015) Exploring the planetary boundary for chemical pollution. Environ Int 78:8–15). Environ Int 82:113. https://doi.org/10.1016/j.envint.2015.04.010

Núñez-Delgado A, Álvarez-Rodríguez E, Fernández-Sanjurjo MJ, Nóvoa-Muñoz JC, Arias-Estévez M, Fernández-Calviño D (2015a) Perspectives on the use of by-products to treat soil and water pollution. Microporous Mesoporous Mater 210:199–201. https://doi.org/10.1016/j.micromeso.2015.02.001

Núñez-Delgado A, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Cutillas-Barreiro L, Nóvoa-Muñoz J, Arias-Estévez M (2015b) Cr(VI) sorption/desorption on pine sawdust and oak wood ash. Int J Environ Res Public Health 12(8):8849–8860. https://doi.org/10.3390/ijerph120808849

Núñez-Delgado A, Romar-Gasalla A, Santás-Miguel V, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Nóvoa-Muñoz JC, Arias-Estévez M (2017) Cadmium and lead sorption/desorption on non-amended and by-product-amended soil samples and pyritic material. Water 9(11):886. https://doi.org/10.3390/w9110886

Paradelo R, Cutillas-Barreiro L, Soto-Gómez D, Nóvoa-Muñoz JC, Arias-Estévez M, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Núñez-Delgado A (2016) Study of metal transport through pine bark for reutilization as a biosorbent. Chemosphere 149:146–153. https://doi.org/10.1016/j.chemosphere.2016.01.087

Paradelo R, Conde-Cid M, Arias-Estévez M, Nóvoa-Muñoz JC, Álvarez-Rodríguez E, Fernández-Sanjurjo MJ, Núñez-Delgado A (2017) Removal of anionic pollutants by pine bark is influenced by the mechanism of retention. Chemosphere 167:139–145. https://doi.org/10.1016/j.chemosphere.2016.09.158

Pyrzynska K (2019) Removal of cadmium from wastewaters with low-cost adsorbents. J Environ Chem Eng 7(1):102795. https://doi.org/10.1016/j.jece.2018.11.040

Pousada-Ferradás Y, Seoane-Labandeira S, Mora-Gutiérrez A, Núñez-Delgado A (2012) Risk of water pollution due to ash–sludge mixtures: column trials. Int J Environ Sci Technol 9:21–29. https://doi.org/10.1007/s13762-011-0014-6

Quintáns-Fondo A, Ferreira-Coelho G, Paradelo-Núñez R, Nóvoa-Muñoz JC, Arias-Estévez M, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Núñez-Delgado A (2016a) F sorption/desorption on two soils and on different by-products and waste materials. Environ Sci Pollut Res 23:14676–14685. https://doi.org/10.1007/s11356-016-6959-8

Quintáns-Fondo A, Ferreira-Coelho G, Paradelo-Núñez R, Nóvoa-Muñoz JC, Arias-Estévez M, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Núñez-Delgado A (2016b) As(V)/Cr(VI) pollution control in soils, hemp waste, and other by-products: competitive sorption trials. Environ Sci Pollut Res 23:19182–19192. https://doi.org/10.1007/s11356-016-7108-0

Quintáns-Fondo A, Fernández-Calviño D, Nóvoa-Muñoz JC, Arias-Estévez M, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Núñez-Delgado A (2017) As(V) sorption/desorption on different waste materials and soil samples. Int J Environ Res Public Health 14(7):803–813. https://doi.org/10.3390/ijerph14070803

Quintáns-Fondo A, Santás-Miguel V, Nóvoa-Muñoz JC, Arias-Estévez M, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Núñez-Delgado A (2018) Effects of changing pH, incubation time, and As(V) competition, on F− retention on soils, natural adsorbents, by-products, and waste materials. Front Chem 6:51–60. https://doi.org/10.3389/fchem.2018.00051

Reddy DHK, Vijayaraghavan K, Kim JA, Yun YS (2017) Valorisation of post-sorption materials: Opportunities, strategies, and challenges. Adv Colloid Interf Sci 242:35–58. https://doi.org/10.1016/j.cis.2016.12.002

Rivas-Pérez IM, Paradelo-Núñez R, Nóvoa-Muñoz JC, Arias-Estévez M, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Núñez-Delgado A (2015) As(V) and P competitive sorption on soils, by-products and waste materials. Int J Environ Res Public Health 12(12):15706–15715. https://doi.org/10.3390/ijerph121215016

Rivas-Pérez IM, Conde-Cid M, Nóvoa-Muñoz JC, Arias-Estévez M, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Núñez-Delgado A (2017) As(V)/Cr(VI) retention on un-amended and waste-amended soil samples: competitive experiments. Environ Sci Pollut Res 24:1051–1059. https://doi.org/10.1007/s11356-016-8015-0

Romar-Gasalla A, Rivas-Pérez IM, Paradelo-Núñez R, Nóvoa-Muñoz JC, Arias-Estévez M, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Núñez-Delgado A (2016) Phosphorus retention on forest and vineyard soil samples, mussel shell, pine-sawdust, and on pyritic, granitic and waste materials. Geoderma 280:8–13. https://doi.org/10.1016/j.geoderma.2016.06.003

Romar-Gasalla A, Nóvoa-Muñoz JC, Arias-Estévez M, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Núñez-Delgado A (2018a) Controlling risks of P water pollution by sorption on soils, pyritic material, granitic material, and different by-products: effects of pH and incubation time. Environ Sci Pollut Res. https://doi.org/10.1007/s11356-018-2267-9

Romar-Gasalla A, Santás-Miguel V, Nóvoa-Muñoz JC, Arias-Estévez M, Álvarez-Rodríguez E, Núñez-Delgado A, Fernández-Sanjurjo MJ (2018b) Chromium and fluoride sorption/desorption on un-amended and waste-amended forest and vineyard soils and pyritic material. J Environ Manag 222:3–11. https://doi.org/10.1016/j.jenvman.2018.05.050

Saka C, Şahin Ö, Küçük MM (2012) Applications on agricultural and forest waste adsorbents for the removal of lead (II) from contaminated waters. Int J Environ Sci Technol 9:379–394. https://doi.org/10.1007/s13762-012-0041-y

Seco-Reigosa N, Bermúdez-Couso A, Garrido-Rodríguez B, Arias-Estévez M, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Núñez-Delgado A (2013) As(V) retention on soils and forest by-products and other waste materials. Environ Sci Pollut Res 20:6574–6583. https://doi.org/10.1007/s11356-013-1730-x

Seco-Reigosa N, Cutillas-Barreiro L, Nóvoa-Muñoz JC, Arias-Estévez M, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Núñez-Delgado A (2014) Mixtures including wastes from the mussel shell processing industry: retention of arsenic, chromium and mercury. J Clean Prod 84:680–690. https://doi.org/10.1016/j.jclepro.2014.01.050

2 Exopolysaccharides: Production and Application in Industrial Wastewater Treatment

Ratna Trivedi

Abstract

In recent decades, polysaccharide molecules of plant, bacterial, and fungal origin have been extensively researched due to their multi-functionality. Various kinds of polysaccharides produced by plants, viz., cellulose, pectin, and starch; algae, viz., agar, alginate, and carrageenan; and bacteria, viz., alginate, dextran, gellan, pullulan, and xanthan gum), are commonly used as food additives for their gelling, stabilizing, or thickening properties (Sutherland IW. Microbiology-SGM 147:3–9, 2001a). Both prokaryotes and eukaryotes are able to produce exopolysaccharides (EPSs); prokaryotes such as eubacteria and archaebacteria and eukaryotes such as phytoplankton, fungi, and algae have now got more research attention (Houghton J, Quarmby J, Stephenson T. Water Sci Technol 44(2):373–379, 2001). Bacteria carry the EPS as their metabolic products which accumulate on the cell surface (Kumar AS, Mody K, Jha B. J Basic Microbiol 47:103–117, 2007a). The composition of EPS has a variety of organic and inorganic substances which have structural variable like either homopolysaccharides such as dextran, mutan, and levan or heteropolysaccharides. Application of various nano material, prepared as bionanoparticles, helpful to treat industrial waste water.

Keywords

Exopolysaccharide · Prokaryotic polysaccharide · Eukaryotic polysaccharide · Bionanopaticles · Industrial waste water treatment

---

R. Trivedi (✉)
Department of Environmental Science, Shree Ramkrishna Institute of Computer Education and Applied Sciences, Surat, Gujarat, India

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_2

2.1 Introduction

In recent decades, polysaccharide molecules of plant, bacterial, and fungal origin have been extensively researched due to their multi-functionality. Various kinds of polysaccharides produced by plants, viz., cellulose, pectin, and starch; algae, viz., agar, alginate, and carrageenan; and bacteria, viz., alginate, dextran, gellan, pullulan, and xanthan gum), are commonly used as food additives for their gelling, stabilizing, or thickening properties (Sutherland 2001a). Both prokaryotes and eukaryotes are able to produce exopolysaccharides (EPSs); prokaryotes such as eubacteria and archaebacteria and eukaryotes such as phytoplankton, fungi, and algae have now got more research attention (Houghton et al. 2001). Bacteria carry the EPS as their metabolic products which accumulate on the cell surface (Kumar et al. 2007a). The composition of EPS has a variety of organic and inorganic substances which have structural variable like either homopolysaccharides such as dextran, mutan, and levan or heteropolysaccharides. Application of various nano material, prepared as bionanoparticles, helpful to treat industrial waste water.

Perhaps, biomolecules from plants now have captured the commercial market for their ease of availability and cost-effective purification process. But renewability, stable cost, and constant and reproducible physicochemical properties of the microbial polysaccharides have provided them an edge over the macromolecules of plant origin, although only few of them have been commercialized so far (Poli et al. 2009; Reichhardt and Cegelski 2014). Exopolysaccharides (EPS) are polymers excreted by some microorganisms as a protective barrier against harmful conditions. Many microbial EPS, such as xanthan or gellan gums, isolated from terrestrial sources are being successfully exploited in several industries. Indeed, EPS can be used in a wide range of biotechnological applications, such as thickening agents, stabilizers, and texturizers in the food industry, flocculating agents in the wastewater treatment industry, or anti-aging molecules in the cosmetics industry.

EPSs have a significant influence on the physicochemical properties of microbial aggregates, including structure, surface charge, flocculation, settling properties, dewatering properties, and adsorption ability. EPSs bind with cells through complex interactions to form a vast net-like structure with plenty of water that protects cells against dewatering (Sutherland 2001a) and the harm of toxic substances. Part of EPS can serve as carbon or energy sources in conditions of nutrient shortage (Banik et al. 2007; Manjamadha and Muthukumar 2016). They also accelerate the formation of microbial aggregates through binding cells closely (Lepek and D'Antuono 2005). Thus, the in-depth study of EPS is a matter of great interest not only in terms of improving our comprehension of biological wastewater treatment, but also improving the efficiency of such treatment through the optimization of operational parameters.

Bacterial cells are capable to produce two different types of extracellular polysaccharides which bind either to the bacterial cell surface tightly, defined as capsular polysaccharides (CPS), or they can be excreted into the extracellular surrounding environment, described as exopolysaccharides (EPS) which can be lightly attached to the bacterial cells or totally detached from the bacteria. A large and growing body of literature has labelled these two types of extracellular polysaccharides with the

Table 2.1 Microbial EPS and its structure

Bacteria	EPS	Chemical structure
Pseudomonas aeruginosa, *Pseudomonas putida*	Alginate	β-1,4-linked mannuronic and α-1,4-linked guluronic acids
Acetobacter xylinum	Bacterial cellulose	β-1,4-linked glucose
Sphingomonas paucimobilis	Gellan	β-d-glucuronic acid-1,4-β-d-glucose-1,4-β-l rhamnose
Leuconostoc mesenteroides	Dextran	α-1,6-linked glucose; some 1,2-, 1,3-, or 1,4-bonds are also present in some dextrans
Alcaligenes faecalis	Curdlan	β-1,3-glucan
Xanthomonas campestris	Xanthan	Linear β-1,4-glucan backbone with β-mannose-1,4-β-glucuronic acid-1,2-α-mannose trisaccharide side Chain
Bacillus polymyxa	Levan	β-2,6-fructan

term exopolysaccharides (EPS) (Broadbent et al. 2003). The main examples of the applications of microbial exopolysaccharides are listed in Table 2.1.

The application of these structural features has great demand in the natural components of bacterial EPS to gain a special interest in recent years in chemistry, medicine, pharmaceuticals, and especially the food industry (Jin et al. 2004). Several functions are attributed to the bacterial EPS such as protecting bacterial cells from desiccation and the environment, antibiotics, phagocytosis, and phage attacks, and they are also believed to play a role in biofilm formation (Kumar et al. 2007b). Besides the role of EPS at the single cell level, they are widely used in the food industry as viscosifying, stabilizing, and emulsifying agents because of their unique physicochemical properties related to their structures (Dhayalan et al. 2017). Dextran, xanthan, gellan, pullulan, yeast glucan, and bacterial alginate are some examples of microbial EPS used in the food industry for decades to improve the physicochemical properties of food formulations (Sutherland 1998). There are many other examples of the technological applications of EPS in food or non-food industries. Recently, EPS also gained special interest after the recent reports showing that EPS may stimulate and modulate the immune system and they may play a role as antitumor, antiviral, anti-inflammatory, and antioxidant agents (Lepek and D'Antuono 2005; Liu et al. 2007).

2.2 Types of EPS

Microbial EPSs are classified into two groups according to their chemical composition, as either homopolysaccharides or heteropolysaccharides, and show a wide diversity in their structures. Homopolysaccharides are composed of the same sugar submits in their repeating unit structure with different linkages (Mikkelsen and Keiding 2002; Mu and Yu 2006). Homopolysaccharides can be part of the capsule layer of Gram-positive and Gram-negative bacteria such as oral *Streptococcus* spp. and *Escherichia* spp.; they can also be secreted to the environment as a slime material like the bacterial cellulose produced by *Acetobacter* spp. One of the most important examples of the microbial homopolysaccharides is dextran produced by *Leuconostoc mesenteroides* which has been found to have a wide range of applications in medicine (Kanmani et al. 2011). Several lactic acid bacteria (LAB) also produce homopolymeric EPS which will be discussed later in this section. Heteropolysaccharides are made of repeating units which are composed of two or more types of sugar subunits, substituted sugars, and other organic and inorganic molecules (Broadbent et al. 2003; Cheng et al. 2011). A general example of microbial heteropolysaccharide is peptidoglycan, which is the main component of bacterial cell walls and is composed of the repeating units of N-acetylglucosamine and N-acetylmuramic acid residues.

The polysaccharides produced by microorganisms can be classified into three main groups according to their location in the cell: (1) cytosolic polysaccharides, which provide a carbon and energy source for the cell; (2) polysaccharides that make up the cell wall, including peptidoglycans, teichoid acids, and lipopolysaccharides; and (3) polysaccharides that are exuded into the extracellular environment in the form of capsules or biofilm known as EPSs (Freitas et al. 2012; Kalogiannis et al. 2003). Exocellular polysaccharides constantly diffused into the cell culture medium are easily isolated, while cell wall and intercellular polysaccharides are more difficult to separate from cell biomass. The intracellular biopolymers are few and have very limited use. The external cellular structure capsule has covalent bonds and cohesive layers while slime is completely excreted into the environment. Extracellular polymers are polysaccharides in more than 95% cases. Unattached EPS production is especially valuable for biotechnological industry as there is no need for costly procedures for removing cell debris.

2.3 Composition and Structure

Carbohydrates and proteins are usually found to be the major components of EPS. Humic substances may also be a key component of the EPS in sludge in biological wastewater treatment reactors, accounting for approximately 20% of the total amount. In addition, lipids, nucleic acids, uronic acids, and some inorganic components have also been found in EPS from various matrixes. Their fractions in EPS depended strongly upon the extraction methods and the sludge origins. The content and compositions of the EPS extracted from various microbial aggregates are reported to be heterogeneous (Sutherland 2001a). The variation in the compositions of the extracted EPS is attributed to many factors, such as culture, growth phase, process parameter, bioreactor type, extraction method, and analytical tool used (Fig. 2.1).

Different numbers of chemical structures of bacterial EPSs are available; in general, they are heteropolysaccharides possessing three or four different monomers organized in groups of a set of 10 or less to give the repeating units. The molecular weight of these polymers is between 1×10^5 and 3×10^5 Da and they are linear too. In addition to monosaccharides, they could possess substituents such as acetate, pyruvate, succinate, phosphate, and sulfate; the presence of uronic acids or ketal-linked pyruvate resulted in polyanionic chains. The most frequent monosaccharides found in EPSs are hexoses,

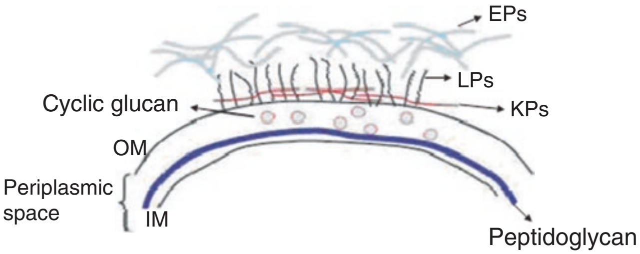


Fig. 2.1 Schematic representation of bacterial surface polysaccharides. *EPS* exopolysaccharides, *KPS* exopolysaccharides attached to the bacterial surface, *LPS* lipopolysaccharides, *IM* cell internal membrane, *OM* cell outer membrane (Lazaridou et al. 2002)

pentoses, uronic acids, and amino sugars which bind each other by 1,4-β or 1,3-β linkages in the strong rigidity polymer structure while the 1,2-α- or 1,6-α linkages are generally present in the flexible polysaccharides (Freitas et al. 2009).

The position in EPS structures is very important to explain the physicochemical and biological properties of these biopolymers and to characterize and in some case to predict the biotechnological applications of the EPS-producer microorganisms or of their bioproducts. Numerous chemical and physical techniques are used to determine the primary structure of EPSs such as chemical degradation and derivatization, in association with chromatographic methods together with mass spectrometry analysis; some are used to determine the sugar composition, their absolute configuration, and the presence and the position of possible substituents (Pan and Mei 2010). With the help of rheological properties of these polymers, the primary conformation can be easily detected. Moreover, secondary configuration regularly takes the form of aggregated helices, and the presence and the absence of specific acyl groups, for example, O-acetyl or O-succinyl esters or pyruvate ketals, can influence the formation of ordered helical aggregates.

2.4 Production of EPS

2.4.1 Conditions for Microbial Production of EPS

Fermentation is a very versatile technique for producing value-added products such as microbial EPS production. All fermentation conditions like medium composition, pH, temperature, aeration, as well as mode of operation are known to have a high impact upon the viability and economics of the bioprocess; their optimization is compulsory in designing a commercial bioprocess (Wilen et al. 2003). Moreover, structural features and related physicochemical and rheological properties of the EPS are largely determined according to the metabolic requirements of the microorganism and also by conditions of the fermentation; therefore, each microbial system should be optimized individually by avoiding generalizations. Fermentation process involves conventional methods like batch, fed-batch, and continuous modes of operations, but in this production, drastic changes in rheological properties of the microbial culture, for example, highly viscous and non-Newtonian broth, may result in great problems in mixing, heat transfer, and oxygen supply (Palaniraj and Jayaraman 2011).

These are the challenges encountered in the microbial production of pullulan and xanthan, but are not encountered in the production of low-viscosity polymers such as levan or in high-temperature processes where thermophiles are utilized as microbial producers. Media for fermentation utilizes almost one-third of the opposed to production costs, and particularly the carbon source which is used as the fermentation feedstock has the greatest cost. Irrespective of whether the production is either at laboratory scale or large industrial scale, media with a high carbon to nitrogen ratio are used owing to the carbon-and energy-intensive nature of the process. Intended to biopolymers with high economic values, consistency in product quality relative to production yield becomes vital, which in turn needs chemically distinct medium conditions. In addition to that, recent efforts are mainly devoted to maintain both product quality and yield by using cost-effective and environmentally friendly production methods that employ inexpensive fermentation substrates (Rijnaarts et al. 1999). In consequence, a wide variety of industrial and agricultural waste and by-products are used in many industrial fermentation products like nutrients such as molasses and syrups, wastewater of olive oil pill, whey of cheese, pomade of various vegetables and fruits, pulp and kernels, lignocellulosic biomass like hall rice and bran, sawdust, and fibers (Poli et al. 2013). Utilization of such complex feedstocks requires intensive research activities for the development of feasible pretreatment, fermentation, and downstream processing techniques. From these, syrups and molasses have long been used for microbial production of various polysaccharides such as xanthan, dextran, pullulan, gellan, and levan due to their high sucrose and other nutrient contents, low cost and ready availability, and ease of storage (Morgan et al. 1990; Kalogiannis et al. 2003; Liu et al. 2004; Poli et al. 2013). Another promising resource is carbon dioxide since it is abundant, renewable, nontoxic, and non-flammable. Microalgae due to their high-CO_2 fixation capacity and fast growth served as established resources in next-generation biofuel technology. Moreover, use of microalgae in EPS production is a quite recent subject with only limited number of reports; however, controlled cultivation systems provide high yield production and also required photobioreactors that are very much expensive and energy intensive when compared with open systems (De Vuyst and Degeest 1999).

Subsequently in the microbial fermentation, the EPS is separated from the culture broth by first eliminating the cellular biomass via centrifugation or filtration. Then, the polymer in clarified medium is precipitated by using a suitable organic solvent like ethanol, acetone, or methanol. The polymer pellet can be dried by lyophilization or heat treatment of obtained crude polymer powders. For higher levels of purity, the pellet is dissolved in suitable solvent (usually water) and then either subjected to additional round of solvent precipitation or dialysis or a combination of these followed by a final drying step (Wingender et al. 1999).

2.4.2 Gene, Genetics, and Gene Expression of Regulation of Microbial Polysaccharide

The production of microbial EPS is usually not confined to just one type of EPS but a mixture of various polymers, each being expressed and produced by a certain gene cluster. Usually, the convenience of the precursors encoded by these genes has a high impact on the yield and structure of the EPS produced by the cell (Parolis et al. 1996).

As a systematic approach for biosynthetic pathways of EPS, microbial genome sequence is considered as a starting point, and from this point of view, next-generation sequencing (NGS) technologies play a vital role by enabling high-throughput genomic data at very high speed with a relatively low cost. Such approaches either aim to elucidate biosynthesis mechanisms, to improve the microbial productivity via strain improvement strategies, or to modify physicochemical and/or rheological properties of the biopolymer by changing its composition, length, or degree of branching (Toksoy Öner 2013).

Current research helps to analysis of a genus *Bifidobacterium* revealed high variability in both the number and organization of the EPS biosynthetic gene by comparative genomics, which in turn suggested that these genes were most probably acquired by horizontal transfer (Gauri et al. 2009). Comparisons of six genomes of *Crocosphaera watsonii* strains were studied with production of high-level EPS, where high-level EPS producers were found to retain the EPS biosynthesis gene clusters (Bench et al. 2013). So from the above study, the location of these gene clusters is usually on the chromosome, whereas in most LAB as well, these genes are found to be confined to plasmids.

Sequence data of a taxonomically close species could also be used for systems-based studies while the whole genome sequence of the EPS-producer microorganism is not available. Construction of metabolic model for levan production by halophilic strain *Halomonas* spp., where first, the available whole genome sequence of a taxonomically close microorganism, *Chromohalobacter salexigens* After it was used (Ateş et al. 2013), as a model for recruitatin and adoptation to the producer strain via integration of the available biochemical, physiological, and phenotypic features of *Halomonas* spp. With metabolic system analysis of this generic metabolic model, significant improvement in levan yields was obtained (Ateş et al. 2011).

EPS Application in Wastewater Treatment

EPSs cover the surface or fill in the interior of cells of microbial aggregates during wastewater treatment of vessels. Li and Ganczarczyk (1990) noted that in the interior of activated sludge flocs with amorphous-phase surrounding cells, the presence of plenty of EPS was observed (Li and Ganczarczyk 1990). This recommends that substrate must pass through the EPS layer for proper biochemical processes to the cells. The substrate efficiency is affected by many factors, viz., mass transfer, pores in granular sludge, and chemical nature of EPS (Liao et al. 2001; Vanhaverbeke et al. 2003). Normally, water has high component diffusion coefficients compared to EPS, which means that EPS may provoked the import of nutrients and the export of metabolic products; as impermeable substances, EPS may prohibit the permeation of dye to cells. EPSs significantly influence the effective diffusion coefficients of substrates; a high level of EPS is not beneficial for substrate mass transfer (Küçükaşık et al. 2011). The permeability of anaerobic granules was found to be lower at a higher level of EPS (Li and Ganczarczyk 1990). However, as EPS can adsorb organic substances and increase their concentration in the region of the cell surface, the role of EPS in mass transfer must be carefully considered.

There are different charged groups in EPS; their composition and content interfere the surface ions of microbial aggregates. Moreover, the physicochemical characteristics of the various components in EPS are not studied properly till today, so they have different effects on the surface charge of aggregates. Frequently, the EPS content had a positive ionic bond on the net negative surface charge so that the total EPS content and the individual components both had a positive effect on the negative charge of sludge, which gives the effects of proteins and humic substances that are the most significant. Liao et al. (2001) reported that the carbohydrate content of EPS had a positive relationship with the net surface charge (Liao et al. 2001), whereas Wang et al. (2005) studied that changes in EPS composition and its surface characterized by sludge which may in the aerobic sludge granulation process as well found that the total EPS content and the protein and carbohydrate contents had a negative effect on the net surface charge of sludge (Vedyashkina et al. 2005). In contrast, the DNA content had no significant effect on either the surface charge or the hydrophobicity of the sludge (Lebeer et al. 2008; Sutherland 2001b).

The ratios between EPS components have a more significant effect on surface charge of microbial aggregates than the content of individual components. The proteins/carbohydrates ratio was found to have a negative effect on net surface charges of sludge, while total EPS composition was found to have no influence. This attributed to the unique charge properties of proteins. The amino groups in proteins are positive and can neutralize the negative charges from carboxyl and phosphate groups and thus decrease the net negative surface charges of sludge.

The role of EPS component in relation to flocculation has also been studied; the microbial aggregates have a tendency to deflocculate after the removal of their surface proteins. However, addition of a small amount of protein-hydrolyzing enzyme to a reactor would lead to the sludge de-flocculation, while dose of a carbohydrate-degrading enzyme caused much less de-flocculation. Nucleic acids may also play an important role in flocculation where bacterial flocculation ability worsened after the degradation of nucleic acids in the EPS of *Rhodovulum* sp., which was treated by nucleic acid hydrolase. Wilen et al. (2003) observed that the flocculation ability of sludge was proportionate with the protein content or adversely proportionate with the humic substance content (Wang et al. 2008). Thus, the production implies that the influence of individual EPS components on the flocculation of microbial aggregates is complex. The ratios of the main EPS components may be more influential on the microbial flocculation (Lebeer et al. 2008). The researchers also observed that readily extracted EPSs are more beneficial for flocculation. In year 2007, Li and Yang observed that the LB-EPS had a negative effect on sludge flocculation and excessive EPS in the form of LB-EPS could weaken cell attachment and result in poor flocculation (Liu et al. 2004).

The theory of microbial cell flocculation can be described using the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) or its extended theories. In the DLVO theory, the total energy of adhesion is the result of the van der Waals attractive forces and the generally repulsive interactions due to the interpenetration of the electrical double layers (Parolis et al. 1999), while the van der Waals forces, polar interactions, electrical double layer interaction, and Brownian movement forces are taken into consideration by the extended DLVO theory. The cell could aggregate and flocculation would occur; the cell kinetics may lead to overcome the total energy barrier in the DLVO curves. This theory also provides an effective way to evaluate the contribution of EPS to production as well as to the sludge flocculation.

EPS can be regarded as key factors in the thickening and dewatering processes of sludge (Hellerqvist and Sweetman 1990; Li and Ganczarczyk 1990). There are major two types of binding mechanisms between water molecules and EPS that are involved: (i) electrostatic interactions and (ii) hydrogen bonds. The electrostatic interactions are active between the permanent functional dipole group of water of the EPS, while hydrogen bonds are active between EPS hydroxyl groups and water molecules. Usually, the pressure filtration is the main means for sludge dewatering. While the specific resistance to or capillary suction time is commonly used to characterize the dewatering ability of sludge through press. An increase in EPS generally leads to a poorer sludge dewatering ability, possibly because the steric force that is generated by EPS prevents contact between cells.

Flocculation in industrial waste due to macromolecules involved in EPS production, when retention of much water in sludge that increase the amount flocs in it. EPSs also have the ability to form a stable gel that prevents water seepage from the pores of flocs, which deteriorates the dewatering ability of sludge, and after the removal of EPS, the sludge dewatering ability would be improved (Chowdhury et al. 2015). However, some studies have shown that sludge dewatering ability improves as the EPS content increases (Li and Ganczarczyk 1990; Houghton and Stephenson 2002). With a higher EPS content, activated sludge had a lower shear sensitivity and lower degree of dispersion, leading to a good dewatering ability. In 2001, Houghton et al. suggested that the content of EPS in sludge had an impact on the dewatering ability of sludge (Houghton et al. 2001). Equally, as the EPS content further increased and exceeded a certain threshold, the water that was retained by the EPS significantly increased, which resulted in a lower sludge dewatering ability (Hidalgo-Cantabrana et al. 2014).

2.4.3 Silver Nanoparticles in EPS Coating

The improved experiments of degradation with our nano-catalysts on EPS coating can be attributed to the following reasons: (i) high surface area of the EPS can adsorb azo dyes; (ii) NaBH4 is expected to act as hydride source, and the AgNPs catalysts are expected to activate the azo nitrogen bond and also to bind with the sulfur and oxygen atoms of the dyes resulting in weakening of azo double bond via conjugation; (iii) large number of oxygen atoms of the EPS could assist in increasing the number of AgNPs; and (iv) EPS networks containing more of hetero atoms are expected to exhibit hydrophilic interactions with azo dyes, which helps in bringing the dye molecules near the catalytic sites.

Progress in nanoscale sciences may provide solution to many of the current problems involving water quality. The use of nanosorbents, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes, and nanoparticle enhanced filtration products and processes resulting from the development of nanotechnology would greatly help to get potable drinking water. Innovations in the development of novel technologies to desalinate water are among the most exciting and promising. The development of novel nanoscale materials and processes for treatment of surface water, ground water, and industrial wastewater contaminated by toxic metal ions, radionuclides, organic and inorganic solutes like pesticides, bacteria, and viruses would be the major environmental contribution of nanotechnology.

Recent studies prove that many of the issues involving potable water quality could be resolved using nanoparticles, nanofiltration, or other nano-materials. Innovative use of nanoparticles for treatment of industrial wastewater is another potentially useful application of nano-materials as many industries generate large amounts of wastewater contaminated with toxic and non-biodegradable effluents. Removal of contaminants and recycling of the contaminated water would provide significant reductions in cost, time, and labor for the industries and increase their eco-friendliness.

2.5 Conclusion

In current era of biotechnology, the application of EPS producing microorganisms in the remediation of environmental effluents is very useful. Biofilm-mediated bioremediation has been found to be a more powerful alternative to bio-remediation with planktonic bacteria as cells growing within a biofilm have greater probabilities of adaptation to various environmental conditions and their subsequent survival. For most industrial advantageous production of biofilms, optimal chemical and physiological conditions, localized solute concentrations and redox potential, allowing cells to improve mineralization processes (Chen et al. 2001). Usually hydrocarbon used in biofilm reactors, heavy metals and large volumes of dilute aqueous solutions such as industrial and municipal wastewater. The probable role of EPS in the removal of heavy metals from the environment is due to their participation in flocculation and aptitude to bind metal ions from keys. A major group of bacteria which are usually found in metal-contaminated wastewaters is sulfate-reducing bacteria (SRB). This group of bacteria has been shown to be extremely efficient in anaerobic degradation of many organic pollutants as well as in the precipitation of heavy metals from wastewater. Other bacteria exhibiting bio-sorption of toxic heavy metals in bioremediation processes include *Enterobacter* and *Pseudomonas* species.

Therefore, the search for greener technologies will probably augment the use of bacterial exopolysaccharide for industrial applications. Thus, the use of bacteria as renewable resource for the production of biopolymers can be greatly advantageous. The current knowledge about bacterial EPS advises that these polymers may cover a broad range of complex chemical structures and consequently diverse properties. Moreover, it is reasonable to anticipate that exopolysaccharides from newer bacteria would provide ample occasions for newer industrial avenues and have chattels different from those already available.

References

Ateş Ö, Toksoy Öner E, Arga KY (2011) Genome-scale reconstruction of metabolic network for a halophilic extremophile, Chromohalobacter salexigens DSM 3043. BMC Syst Biol 5:12

Ateş Ö, Arga KY, Toksoy Öner E (2013) The stimulatory effect of mannitol on Levan biosynthesis: lessons from metabolic systems analysis of Halomonas smyrnensis AAD6(T). Biotechnol Prog 29:1386–1397

Banik RM, Santhiagu A, Upadhyay SN (2007) Optimization of nutrients for gellan gum production by Sphingomonas paucimobilis ATCC-31461 in molasses based medium using response surface methodology. Bioresour Technol 98:792–797

Bench SR, Heller P, Frank I, Arciniega M, Shilova IN, Zehr JP (2013) Whole genome comparison of six Crocosphaera watsonii strains with differing phenotypes. J Phycol 49:786–801

Broadbent JR et al (2003) Biochemistry, genetics, and applications of exopolysaccharide production in Streptococcus thermophilus: a review. J Dairy Sci 86(2):407–423

Chen Y, Yang H, Gu G (2001) Effect of acid and surfactant treatment on activated sludge dewatering and settling. Water Res 35:2615

Cheng KC, Demirci A, Catchmark JM (2011) Pullulan: biosynthesis, production, and applications. Appl Microbiol Biotechnol 92:29–44

Chowdhury IH, Ghosh S, Roy M, Naskar MK (2015) Green synthesis of water-dispersible silver nanoparticles at room temperature using green *carambola* (star fruit) extract. J Sol-Gel Sci Technol 73:199–207

De Vuyst L, Degeest B (1999) Heteropolysaccharides from lactic acid bacteria. FEMS Microbiol Rev 23(2):153–177

Dhayalan M, Denison MIJ, Jegadeeshwari AL, Krishnan K, Gandhi NN (2017) In vitro antioxidant, antimicrobial, cytotoxic potential of gold and silver nanoparticles prepared using *Embelia ribes*. Nat Prod Res 31:465–468

Freitas F, Alves VD, Pais J, Costa N, Olivera C, Mafra L et al (2009) Characterization of an extracellular polysaccharide produced by a pseudomonas strain grown on glycerol. Bioresour Technol 100:859–865

Freitas AC, Rodrigues D, Rocha-Santos TAP, Gomes AMP, Duarte AC (2012) Marine biotechnology advances towards applications in new functional foods. Biotechnol Adv 30:1506–1515

Gauri SS et al (2009) Enhanced production and partial characterization of an extracellular polysaccharide from newly isolated Azotobacter sp. SSB81. Bioresour Technol 100(18):4240–4243

Hellerqvist CG, Sweetman BJ (1990) Mass spectrometry of carbohydrates. In: Smelter CH, Throck Watson J (eds) Methods of biochemical analysis. Wiley-Interscience, Hoboken, NJ, pp 91–143

Hidalgo-Cantabrana C, Sánchez B, Milani C, Ventura M, Margolles A, Ruas-Madiedo P (2014) Exopolysaccharide biosynthesis in Bifidobacterium spp.: biological functions and a genomic overview. Appl Environ Microbiol 80:9–18

Houghton JI, Stephenson T (2002) Effect of influent organic content on digested sludge extracellular polymer content and dewaterability. Water Res 36:3620–3628

Houghton J, Quarmby J, Stephenson T (2001) Municipal wastewater sludge dewaterability and the presence of microbial extracellular polymer. Water Sci Technol 44(2):373–379

Jin B, Wilen BM, Lant P (2004) Impacts of morphological, physical and chemical properties of sludge flocs on dewaterability of activated sludge. Chem Eng J 98:115–126

Kalogiannis S, Iakovidou G, Liakopoulou-Kyriakides M, Kyriakidis DA, Skaracis GN (2003) Optimization of xanthan gum production by Xanthomonas campestris grown in molasses. Process Biochem 39:249–256

Kanmani P et al (2011) Production and purification of a novel exopolysaccharide from lactic acid bacterium Streptococcus phocae PI80 and its functional characteristics activity in vitro. Bioresour Technol 102(7):4827–4833

Küçükaşık F, Kazak H, Güney D, Finore I, Poli A, Yenigün O et al (2011) Molasses as fermentation substrate for levan production by Halomonas sp. Appl Microbiol Biotechnol 89:1729–1740

Kumar AS, Mody K, Jha B (2007a) Bacterial exopolysaccharides – a perception. J Basic Microbiol 47:103–117

Kumar AS, Mody K, Jha B (2007b) Bacterial exopolysaccharides--a perception. J Basic Microbiol 47(2):103–117

Lazaridou A, Biliaderis CG, Roukas T, Izydorczyk M (2002) Production and characterization of pullulan from beet molasses using a nonpigmented strain of Aureobasidium pullulans in batch culture. Appl Biochem Biotechnol 97:1–22

Lebeer S, Vanderleyden J, De Keersmaecker SC (2008) Genes and molecules of lactobacilli supporting probiotic action. Microbiol Mol Biol Rev 72(4):728–764

Lepek CV, D'Antuono A (2005) Bacterial surface polysaccharides and their role in the rhizobia-legume association. Lotus Newslett 35:93–105. (For figure-1)

Li DH, Ganczarczyk JJ (1990) Structure of activated sludge flocs. Biotechnol Bioeng 35:57–65

Liao BQ, Allen DG, Droppo IG, Leppard GG, Liss SN (2001) Surface properties of sludge and their role in bioflocculation and settleability. Water Res 35:339–350

Liu YQ, Liu Y, Tay JH (2004) The effects of extracellular polymeric substances on the formation and stability of biogranules. Appl Microbiol Biotechnol 65:143–148

Liu Y, Yang CH, Li J (2007) Influence of EPS on Pseudomonas aeruginosa transport and deposition profiles in porous media. Environ Sci Technol 41:198–205

Manjamadha VP, Muthukumar K (2016) Ultrasound assisted synthesis of silver nanoparticles using weed plant. Bioprocess Biosyst Eng 39:401–411

Mikkelsen LH, Keiding K (2002) Physico-chemical characteristics of full scale sewage sludges with implication to dewatering. Water Res 36:2451–2462

Morgan JW, Forster CF, Evison LM (1990) A comparative study of the nature of biopolymers extracted from anaerobic and activated smudges. Water Res 6:743–750

Mu Y, Yu HQ (2006) Biological hydrogen production in a UASB reactor with granules. I:physicochemical characteristics of hydrogen-producing granules. Biotechnol Bioeng 94:980–987

Palaniraj A, Jayaraman V (2011) Production, recovery and applications of xanthan gum by Xanthomonas campestris. J Food Eng 106:1–12

Pan D, Mei X (2010) Antioxidant activity of an exopolysaccharide purified from Lactococcus lactis subsp. lactis 12. Carbohydr Polym 80(3):908–914

Parolis H, Parolis LAS, Boan IF, Rodrıguez-Valera F, Widmalm G, Manca MC et al (1996) The structure of the exopolysaccharide produced by the halophilic archaeon Haloferax mediterranei strain R4 (ATCC 33500). Carbohydr Res 295:147–156

Parolis LAS, Parolis H, Paramonov NA, Boan IF, Anton J, Rodrıguez-Valera F (1999) Structural studies on the acidic exopolysaccharide from Haloferax denitrificans ATCC 35960. Carbohydr Res 319:133–140

Poli A, Kazak H, Gürleyendag B, Tommonaro G, Pieretti G, Toksoy Öner E et al (2009) High level synthesis of Levan by a novel Halomonas species growing on defined media. Carbohydr Polym 78:651–657

Poli A, Nicolaus B, Denizci AA, Yavuzturk B, Kazan D (2013) Halomonas smyrnensis sp. nov., a moderately halophilic, exopolysaccharide-producing bacterium from Camalti Saltern area, Turkey. Int J Syst Evol Microbiol 63:10–18

Reichhardt C, Cegelski L (2014) Solid-state NMR for bacterial biofilms. Mol Phys An Int J at Interface Between Chem Phys 112:887–894

Rijnaarts HHM, Norde W, Lyklema J, Zehnder AJB (1999) DLVO and steric contributions to bacterial deposition in media of different ionic strengths. Colloids Surf B: Biointerfaces 14:179–195

Sutherland IW (1998) Novel and established applications of microbial polysaccharide. Trends Biotechnol 16:41–46

Sutherland IW (2001a) Biofilm exopolysaccharides: a strong and sticky framework. Microbiology-SGM 147:3–9

Sutherland IW (2001b) Microbial polysaccharides from gram-negative bacteria. Int Dairy J 11:663–674

Toksoy Öner E (2013) Microbial production of extracellular polysaccharides from biomass. In: Feng Z (ed) Pretreatment techniques for biofuels and biorefineries. Springer, Berlin, pp 35–56

Vanhaverbeke C, Heyraud A, Mazeau K (2003) Conformational analysis of the exopolysaccharide from Burkholderia caribensis strain MWAP71: impact of the interaction with soils. Biopolymers 69:480–497

Vedyashkina TA, Revin VV, Gogotov IN (2005) Optimizing the conditions of dextran synthesis by the bacterium Leuconostoc mesenteroides grown in a molasses-containing medium. Appl Biochem Microbiol 41:361–364

Wang Y et al (2008) Physicochemical properties of exopolysaccharide produced by Lactobacillus kefiranofaciens ZW3 isolated from Tibet kefir. Int J Biol Macromol 43(3):283–288

Wilen BM, Jin B, Lant P (2003) The influence of key chemical constituents in activated sludge on surface and flocculation properties. Water Res 37:2127–2139

Wingender J, Neu TR, Flemming HC (1999) What are bacterial extracellular polymeric substances? In: Wingender J, Neu TR, Flemming HC (eds) Microbial extracellular polymeric substances: characterization, structures and function. Springer, Berlin/Heidelberg, pp 1–18

3

Treatment Technologies for Addressing the Removal of Industrial Effluents Affecting the Quality of Ganges River in Eastern Part of Uttar Pradesh, India

Sumedha Shah and Abha Mishra

Abstract

India has emerged as a hub for research and development and is ready for escalating to fourth industrial revolution. The fourth level revolves around fusion of technologies for elevating the upcoming manufacturing techniques. Industrialization has helped India to flourish and grow economically among the other developing countries. With all the advantages of increase in industries and production, there comes up the problem of increase in pollutants and contaminants that are discharged untreated. The various sectors of industries in India include textile, cement, mining, food processing, chemical, steel, and dairy. They produce a mixture of toxic and nontoxic pollutants that may or may not be persistent in nature. These pollutants are majorly carcinogenic or become one over their due course of time if not treated. The text focuses on treatment technologies of waste water in the eastern part of Uttar Pradesh, an industrial state in India, where most of the industries are by the side of Ganges River. These industries generate significant amount of waste most likely being chemical and synthetic dyes, heavy metals, and pesticides which are persistent pollutants. The treatment of effluent is essential to stabilize the BOD and COD and reduce presence of heavy metals in river water. The various treatment technologies are used individually or in combination to have effective retaliation and applicability.

Keywords

Ganges · Effluent treatment · Physicochemical treatment · Microalgae · Heavy metal removal

---

S. Shah · A. Mishra (✉)
School of Biochemical Engineering, Indian Institute of Technology (B.H.U), Varanasi,
Uttar Pradesh, India
e-mail: abham.bce@itbhu.ac.in

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_3

3.1 Introduction

The industrialization has come a long way since its incubation. Its impact can be seen in various aspects of life, whether making our lives easy by handling day-to-day work or introducing rapid processes. Manufacturing products in enormous quantities have now become more accessible with research and development in the respective fields. The optimized processing leads to an increase in both finished products and the effluent volume. The poor balance between rapid industrialization and appropriate environmental measures in developing countries leads to increased release of chemicals to both terrestrial and aquatic ecosystem. The effluents consist of undesirable components that are non-degradable and toxic to the environment. The composition of effluent depends upon the industry it is related and the degree of pre-treatment it has gone through before releasing it to nearby land or water body. High COD, BOD, suspended solids, and heavy metals are the most common parameters for assessment of waste water. The persistent nature of the effluents leads to their accumulation in flora and fauna. The effluent gets accumulated over some time and burdens ecosystem. Effluent streams released to nearby rivers or lands affect the agriculture nearby as farmers use river water for irrigation. Thus, the toxic components enter the food chain affecting the consumers directly. Once they have sneaked into the food chain, they get accumulated and even cause fatal effects on living organisms. They degrade the quality of water and leave it inappropriate for any further use.

3.2 Types of Effluent Composition and Industries

3.2.1 Dairy Industry

Among the food industry, dairy is responsible for the significant contribution to effluent in terms of both organic loading and effluent volume (Clarke and Steinle 1995; Grismer et al. 2002; Baskaran et al. 2003; Kushwaha et al. 2010). The organic load is mainly the milk solids and protein from the industry, implying loss to the industry daily (Baskaran et al. 2003). The organic load mostly comprised of proteins, lipids, and carbohydrates owing to high BOD, COD, suspended solids, and grease contents which need treatment along with handling the fluctuations in flow rates due to discontinuity in production cycles of various products (Britz et al. 2006).

The dairy industry is centralized around the conversion of raw milk into various products such as pasteurized milk, sour milk, yogurt, cottage cheese, cream, butter, cheese, ice cream, milk and whey powders, and many more desserts (Rosenwinkel et al. 2005; Tsachev 1982; Britz et al. 2006; Nadais et al. 2010; Carvalho et al. 2013; Karadag et al. 2015).

The fact that the industry is diversified in dimensions such as product processing, handling, and packaging, it creates wastes of discrete quality and quantity which need disposal treatments.

3.2.2 Pulp and Paper Industry

Paper industry is among the oldest industries that flourished since 105 A.D., and since then, its consumers have increased. Paper has come a long way in usefulness and is not limited by its use in writing surface; it finds application in packaging, toiletries, and everyday chores. This industry is considered as the major consumer of natural resources such as wood, water, and energy and is among the critical contributing industries to pollution (Thompson et al. 2001). The use of timber in the UK for pulp and paper industry is expected to reach 15 million cubic meters by the end of 2020. The pulp and papermaking process is highly water intensive, and approximately 200 m^3/ton of water is used for making pulp alone (Cecen et al. 1992). It ranks third in freshwater withdrawal after primary metal and chemical industries. The wastes from pulping and papermaking are different (Billings and DeHaas 1971); the waste water from pulp is heavily loaded with organic matter containing dissolved wood-derived components. The color of final discharge is different in both pulping and papermaking; the presence of lignin imparts color in pulping, and use of dyes in making colored paper gives color to the effluent of papermaking (Thompson et al. 2001). The organic pollutants from pulping are incinerated. The wastes from the industry fall in four primary categories, i.e., gases, effluents, particulates, and solid wastes, which cause substantial damage to the water as the effluent is high in BOD, COD, chlorinated compounds such as adsorbable organic halides (AOXs), suspended solids, tannins, lignins, and sulfur compounds (Ali and Sreekrishnan 2001). The varied nature of pollutants such as natural (wood extracts – tannins, lignins, resin acids) and xenobiotic (furans, dioxins, chlorinated lignins) makes the mill effluent “a nest to waste chemicals” (Peck and Daley 1994). The pollutants such as polychlorinated dibenzodioxins and dibenzofurans are known as persistent organic pollutants (POPs) as they are defiant to degradation and they have a persistent nature (Star 2006). The effect of these effluents on aqautic life can be observed in impaired liver function (Oikari and Nakari 1982). DNA-impairing agents such as dioxins and furans induce genetic defects and cancer that run down in heredity (Brusick 1980; Loprieno 1982; Easton et al. 1997); dioxins are known “human carcinogens” by the World Health Organization (Water and Organization 2004). The effluent imparts a black/brown color to the receiving water bodies. They increase temperature of water and force decreased photosynthesis leading to decrease in dissolved oxygen concentration (Kringstad and Lindström 1984).

3.2.3 Leather Industry

Leather is a seasoned enterprise and finds its presence in upholstery, shoes manufacturing, clothes, gloves, leather goods, and others. It is a prominent industry in terms of export earnings and growth and is always eyed upon for its products. The transformation of hides/skin to commercial product takes into account a combination of chemical and mechanical treatments. The chemicals used are majorly acids, alkalis, hazardous salts, solvents, etc., in aqueous phase. The level of industry ranging from cottage industry to heavy industry depends upon the type of leather produced by tanning of animal skin (Heidemann, Heidemann 1993). The types of leather are:

- Vegetable-tanned leather (Madhan et al. 2001)
- Chrome-tanned leather (Heidemann 1993; Chagne et al. 1996)
- Aldehyde-tanned leather (Serra et al. 1991; Wojdasiewicz et al. 1992)
- Synthetic tanned leather (GUPTA 1980)
- Alum-tanned leather (Montgomery 1986)

3.2.4 Carpet

India has emerged as the major exporter of carpet in international business due to the synergistic effect of craftsmanship and advancement in manufacturing techniques. Manufacturing of a carpet leaves behind ample amount of toxic effluent to the nearby water bodies. The visible pollutant in the effluent is colored compounds, i.e., dyes and inorganic pigment, where color is contributed by tannin and lignin used in industries (Clarke and Steinle 1995). The dyes can be of varied types such as azo, sulfur, reactive, cationic acid, or vat dye (Raghavachary 1997). Dyes get anchored to the fiber by the aromatic compound chromogen, most widely used being azo dye followed by anthraquinone. Another class of dyes is the one based on the application on textiles such as acid, reactive, metal-complex, disperse, vat, mordant, direct, basic, and sulfur dyes (Vandevivere et al. 1998). Dyes are designed to withstand degradation, and this becomes a problem when the same is a part of the effluent from the industry since uptake rate of dyes is 30–70% and the rest is eliminated. A few dyes are reported to be aerobically degradable (Shaul 1987; Ganesh et al. 1994; Pagga and Taeger 1994; Field et al. 1995). Their removal is of major concern due to carcinogenicity and toxicity they cause to the ecology due to the presence of benzidine, naphthalene, and other aromatic compounds which can get transformed due to microbial metabolism. Apart from the visible pollutants like dyes, persistent organics called dyeing and finishing auxiliaries like polyacrylates, phosphonates, sequestering agents, and lignin are also present. Azo dyes when they interact with the ecosystem convert the azo group to aromatic amines and bioaccumulates, causing toxic effects on aquatic life and mutagenic effect on humans (Banat et al. 1996). Azo dye causes hypopigmentation as it inhibits the activity of tyrosinase enzyme resulting in inhibition of melanin synthesis (Dubey et al. 2007).

3.2.5 Mining and Heavy Metal Industry

Originally, the effluents released to the nearby rivers are loaded with high levels of pollutants, and when the industry is heavy metal based, the level of pollutants multiplies. Heavy metals are a group of metallic element with comparatively high density and toxicity in low concentration (Lenntech 2004). The effluent consists a substantial amount of heavy metals which is persistent in nature and causes biomagnification and toxicity to the aquatic life. These metals find their way in the food chain as they are consumed by the aquatic organisms due to high solubility; upon entering the human body, they get accumulated to high extent and have carcinogenic effects. Zinc, copper, nickel, mercury, cadmium, lead, and chromium are the most harmful heavy metals. Copper, nickel, and zinc when present in little quantity in soil promote cell growth of microbial flora by acting as a cofactor unit of enzymes, structural proteins, and ionic balance in cells (Kosolapov et al. 2004). However, a massive amount of the heavy metals degrade the quality of soil by having a crucial effect by interfering the biochemical processing such as nitrogen fixation, assimilation, and degradation of organic residues to release nutrients carried out by microbial species present in the soil leading to alteration in ecological balance (Brookes 1995; Bååth et al. 1998). Heavy metals are easily taken up by plants from polluted soil and accumulate in their tissues. Both herbivores and carnivores get effected by the consumption of heavy metals in food chain, and its accumulation continues to increase (Garbarino et al. 1995; Habashi 1999; Horsfall Jr et al. 1999; Peplow 1999; Trüby 2003).

Renal dysfunction, gastrointestinal disorders, diarrhea, tremor, paralysis, vomiting, and lung diseases are some of the fatal effects posed by the unintentional consumption of heavy metals. Some may even have chronic and carcinogenic effects on consumers irrespective of the quantity, thus leaving metal poisoning effect on humankind.

3.3 Industries in Uttar Pradesh and Effluent Composition

Uttar Pradesh is the most populous state of India, with approximately 200 million inhabitants. Being the fourth most industrialized state of the country, it attracts people from all over the country in search of occupation. Though the presence of industries in the state provides economic strength to the country, repercussions can be observed in terms of environmental depletion that succeeds it. The industries are based on leather, handloom, brass, heavy metal, diesel electric locomotive, and limestone mining.

India is an agriculture-based country with a good requirement of water for irrigation, and as the water level goes down, the waste water from nearby industries is used for irrigation. This contaminates the soil and decreases its nutrient quality, and when plants are cultivated in these terrains, they accumulate the impurities affecting crop quality and subsequently human and animal health on consumption.

3.3.1 Heavy Metal Contamination

Uttar Pradesh has a substantial reserve for mineral and heavy metals owing to the economy of the state. Coal, dolomite, diaspore, sulfur, magnesite, pyrophyllite, silica sand, and limestone are present in various regions of the area. A study conducted by Yadav et al. (2013) in the region of Naini situated at Allahabad, now Prayagraj, investigated the concentration of metals such as lead, zinc, cadmium, iron, copper, and nickel in waste water used for irrigation, soil, and cultivated vegetables grown on the land with prolonged usage of treated and untreated waste water for irrigation. Indian standard guidelines were used to measure and compare the level and potential hazards to human health. Most of the discharged effluent is untreated and flushed out through open drains which contaminates the nearby water and soil.

Another investigation carried out by Gowd et al. (2010) in the region of Kanpur and Unnao district of Uttar Pradesh studied the levels of various contaminations in the area due to industries like tannery, cotton and wool mills, and fertilizer and arm manufacturing-based industries. Chromium from tannery waste is converted from less toxic trivalent form to highly toxic hexavalent form due to the varying environmental conditions when discharged in the soil untreated (Anderson 1999; Ansari et al. 2000; Alloway 2012). Their study was aimed at assessment of level of contamination of soil with respect to the average concentration of toxic metal in the region which helps in assimilation of possible industrial sources of contamination and its geographical pattern in polluting the soil. Various indices such as geo-accumulation, normalized enrichment factor, contamination factor, and degree of contamination were used for estimation. The contamination is no longer restricted to the land it was dumped into; rather, it reaches the groundwater level due to leaching. Many samples that were tested in the study were found to exceed the international threshold level which can be seen by presence of high level of Cd and Zn in the soil directing toward the possible reason being the direct dumping of effluent in large amount to the soil without any pretreatment.

3.3.2 Tannery and Textile Industry

Kanpur is called as the “Leather City” of Uttar Pradesh. During the tenure of April to October, 2018, India stood as the major exporter of leather with a worth of US $3.05 (IBEF). There are more than 2500 tanneries in the country, and 80% of them are based on chrome tanning process. The tanneries are situated in the banks of Ganga River with annual processing of 75000 tonnes of cow and buffalo hides. The hides are processed mainly to hard leather and production of saddles. The waste water discharged is high in chromium (Ramasami 1999; Gupta and Sinha 2006).

According to Al Jazeera, a reputed news channel, Kanpur was the most populated city of North India in 2013. The tanneries situated in the city produce 30 crore liters of waste water to Ganga with the capacity of treatment plant being 17 crore liters/day only and dump 400 tons of solid waste on a daily basis.

The effluent from tannery is a complex mixture of hydrolyzed collagen and fats derived from the skin. Natural and synthetic tannins, aldehydes, and quinones are other organics used in tannery along with aliphatic amines, non-ionic surfactants, and pigments (Ates et al. 1997) (Cassano et al. 2001; Di Iaconi et al. 2002). These effluents cause mutagenic and genotoxic effects (Alam et al. 2009). These contaminants are difficult to detect in the effluent stream as they are present in diminished amount; however, extraction processes are helpful in detection for evaluation of water sample (Umbuzeiro et al. 2001; Courty et al. 2004).

The presence of chromium in water with quantity as low as 0.1 mg/l is toxic to humans (UNIDO 2005); however, it has been found to reach a level of 0.93 mg/l in groundwater samples from tannery (Deepali and Gangwar 2010). Skin contact may cause various skin allergies further resulting in swelling of the skin (Martin and Griswold 2009).

Analyzing Ganga in terms of the physicochemical parameters when it enters Kanpur and leaves it, Khwaja et al. (2001) found that quantity of pollutants exceeds as the river passes the city. The upstream site chosen for sampling was Bithoor, where no tanneries are situated, and downstream site was Jajmau which is the hub for tanneries. High levels of chromium were found in the river with subtle amounts of sulfides and phenols. The surface chromium concentration in downstream site is tenfold higher than the upstream site, and subsurface concentration of chromium is comparatively equal in both sites. The sediment analysis reveals that the surface chromium is mainly in residual fraction in upstream site and bound to Fe-Mn oxide at downstream site concluding that the sediments of chromium may not be threatening. However, most of the physicochemical parameters assessed were found to be quite high with respect to the limits in Indian Standards IS-10500 (1983) for potable water.

Katiyar (2011) examined the Ganga river at different sites in varied seasons such as summer, winter, and monsoon to deduce the impact of tanneries in groundwater such as bore well usually used for drinking and other household purposes. Most of the free metal ions become part of sediment, and very few stay dissolved in the stream. For examination, the sites chosen were upstream and downstream of the river at Jajmau and one site being the discharge site. Alkalinity was assessed and was found higher in downstream site and dumping site during summers when compared to the prescribed level of Bureau of Indian Standards [BIS] due to the excess evaporation of water. High level of alkalinity in water gives bitter taste on consumption and limits its usability for domestic and livestock purposes. The dissolved oxygen [DO] is an important factor in deciding the consumable quality of water. The discharge site had low DO when compared to upstream site; however, it was high during monsoon and winter due to dilution by fresh water. BOD and COD at the discharge site were high round the year due to high organic load. The Cr level was comparatively equal in both sediment and ground water sample at discharge point during summers. The high chromium levels are affecting almost 4.67 lacs of people residing around the area causing diseases like skin lesions, gastrointestinal problems like ulcers, and respiratory problems.

3.3.3 Carpet and Dyes

Bhadohi is the hub of carpet industry in Uttar Pradesh. Several textile industries are located in the area and produce sumptuous amount of wastes each day. The untreated waste water released from the industry is directly used for irrigation. The dyes used when flushed in the river stream impart color and thus hinder light penetration causing disturbance in photosynthesis affecting aquatic life (Van der Zee and Villaverde 2005). The increased organic load in effluent flushed to river water shows negetive effect on biotic of water due to the soluble metal ions and leads to toxicity in marine life.

3.3.4 Pesticides

Organochlorine and organophosphorus are the two classes of pesticides that are majorly used in agriculture. Organochlorine-based pesticides such as DDT are highly toxic and affect the quality of soil as they are non-biodegradable and get concentrated through food chains and cause magnified accumulation, compared to which organophosphorus pesticides are easily degradable. Most of the developed countries have restricted the use of these non-degrading pesticides as they cause harm to both nature and man. In contrast to developed countries, developing countries still use cheap pesticides consisting of DDT, which are easily available and accessible. Pesticide residues reach water bodies due to surface runoff, leaching, and disposal of empty containers. It shows a negative effect on the water quality and thus impacts humans and livestock. The problem is more serious in the countries where the population is dependent upon groundwater as the prime source of water (Spliid and Køppen 1998; Tuxen et al. 2000).

A study done in Kanpur showed that Ganga River is polluted with HCH, dieldrin, and malathion with limits above than that prescribed by EC drinking water quality standards. Both the surface and groundwater show presence of these pesticides attributed to the intensive agricultural practices that take place along the Gangetic Plains in the area (Sankararamakrishnan et al. 2005).

3.4 Treatment Technology

3.4.1 Physicochemical Methods

3.4.1.1 Adsorption

Adsorption is a phenomenon of segregation of adsorbate from aqueous phase on a solid surface (Mohan and Karthikeyan 2004). The process depends on factors like adsorbate-adsorbent interaction, surface area of adsorbent, particle size, contact time, pH, and temperature (Ravi Kumar et al. 1998). Activated carbon, bagasse, wood chips, and peat have been used for effluents from textile and tannery industries for removal of acid and basic and direct dyes. Activated carbon is also useful in the removal of heavy metals such as nickel (Shim et al. 1996), cadmium (Ouki and Neufeld 1997), chromium (Leyva-Ramos et al. 2005), copper (Monser and Adhoum 2002), and zinc (Ramos et al. 2002).

Bio-adsorbents such as dry maize cob, rice husk, and citrus peel in powdered form were analyzed for effective removal of dye precisely Direct Blue 199 from effluent stream, and it showed promising results. However, the increasing dose of adsorbent decreased the dye uptake (mg/g) at equilibrium (Saroj et al. 2015).

3.4.2 Chemical Precipitation

Heavy metal removal from industrial effluent widely uses chemical precipitation (Benefield and Morgan 1990; Ku and Jung 2001). The chemicals react with dissolved metal ions and form insoluble precipitates when adjusted to high alkaline pH (Wang et al. 2005); the formed precipitates are then removed by other primary processes such as filtration and sedimentation (Fu and Wang 2011). Chemical precipitation is carried out by hydroxide precipitation (using lime) (Kurniawan et al. 2006) and sulfide precipitation.

Charerntanyarak (1999) has reported the removal of zinc, manganese, and cadmium cations with metal concentration of 450, 150, and 1085 mg/L in batch-continuous system when lime precipitation was employed. Hydroxide precipitation has wide acceptability as lime is easily available in many countries at low prices. Another addition to this lime precipitation is use of fly ash as seed material (Chen et al. 2009); the size of precipitate increased and heavy metal removal efficiency improved significantly when used in fly-ash-lime carbonation treatment (Fu and Wang 2011). Alum, iron salts, and organic polymers when used as coagulants, enhance the process and the same studies were made by Charerntanyarak (1999), to treat synthetic waste water containing zinc, cadmium, magnesium, and manganese.

Sulfide precipitation unlike hydroxide precipitation is not pH dependent; it can work over a large range of pH since sulfide precipitates are not amphoteric and the sulfide metal complex has low solubility. The sludge formed is easily removed as it is thick (Fu and Wang 2011). Copper, cadmium, and lead removal was investigated by Özverdi and Erdem (2006) using pyrite and synthetic sulfide.

3.4.3 Oxidative Processes

The process is used for decolorization, using H_2O_2 as the main oxidizing agent. The methods of decolorization depends on the activating agent H_2O_2 (Slokar and Le Marechal 1998).

3.4.3.1 Fenton's Reagent

This chemical method is applicable for contaminants that are resistant to biological treatments (Slokar and Le Marechal 1998). It is majorly used for dye decolorization in textile effluent. It uses hydrogen peroxide for removal of both soluble and insoluble dyes by chemical sorption or bonding (Pak and Chang 1999).

3.4.3.2 Ozonation

Ozone is highly instable and degrades chlorinated hydrocarbon, phenol, and aromatic compounds (Lin and Lin 1993; Xu et al. 1999). This method does not produce any sludge, and dosage depends on the total impurities removal (Ince and Gönenç 1997). The method is preferred for dye molecules comprising of double bonds in them (Slokar and Le Marechal 1998). Since ozone is in gaseous state, its application does not load the sludge (Robinson et al. 2001).

3.4.3.3 Photochemical

Dye molecules are reduced to CO_2 and H_2O by the action of ultraviolet radiation for activation of H_2O_2. Sludge and odor formation is prevented in this technique (Robinson et al. 2001).

3.4.3.4 Electrochemical Destruction

This method does not use any chemical for dye breakdown, thus removing the problem of sludge formation and handling. The metabolites that are obtained are not toxic and can be released to the river without any further treatment (Öğütveren and Koparal 1994; Pelegrini et al. 1999).

3.5 Membrane Filtration

This method is used for removal of both dye and heavy metal from the effluent. The continuous removal of dye from waste water can be achieved by using this process (Mishra and Tripathy 1993; Xu et al. 1999). Ultrafiltration, reverse osmosis, nanofiltration, and electrodialysis are the most extensively used filtration methods for the removal of heavy metals from the effluent. Resistance to adverse physical conditions like temperature, chemicals, and microbial attack makes the method widely acceptable.

3.6 Biological Methods

3.6.1 Biomass-Packed Column Reactor

Formaldehyde-urea mixture cross linked *with Spirogyra neglecta* was prepared as column for absorption of metal from waste water. Effluents from carpet industry, paper mill, and electroplating industry were treated using this column. Concentration of metal in the effluent, height of bed, and influent flow rate play a major role in estimation of saturation of column and its breakthrough. However, this column seems promising in removal of metal ions (Singh et al. 2012).

3.6.2 Biofilm Reactor

Anaerobic biofilm reactor is useful as it has high loading capacities and reduced startup time when compared to conventional anaerobic treatment (Zellner et al. 1987). Karadag et al. (2015) reviewed various anaerobic biofilm reactors for their application in treatment of dairy waste water. They concluded with anaerobic film reactors being the most favored among all due to their successful operating capability in high organic loading and efficient COD removal. The biofilm reactors are tested only under mesophilic conditions; sufficient data is not available for their performance in ambient and thermophilic conditions. The hybrid systems such as buoyant film bioreactor have high methane production and efficient COD removal.

3.6.3 Microalgae Bioreactor

Microalgae assimilate the waste water components and use them as nutrients for growth, thus reducing the BOD and COD of the effluent (Bich et al. 1999). The size of microalgae is beneficial as it provides large area and elevates the nutrient uptake rate; the process is termed as phycoremediation (Chinnasamy et al. 2010). Textile waste water consisting of dyes has been reported to be treated with Chlorella vulgaris which were moderately polluted; significant color and COD reduction were observed (El-Kassas and Mohamed 2014).

Heavy metals in waste water are easily taken up by microalgae by forming a peptide-heavy metal complex which reaches vacuoles to separate from cytoplasm and neutralizes the toxic effects. *Desmodesmus pleimorphus* was found suitable for the removal of zinc ion in Portugal (Monteiro et al. 2009). Various other heavy metal contaminants such as manganese, cadmium, arsenic, nickel, copper, and iron were removed by Spirulina platensis (Zainal et al. 2012).

Low energy requirement, little sludge production, and low greenhouse gas emissions are some of the most attractive features of microalgae treatment over other biological methods in treating waste water (Udaiyappan et al. 2017).

3.6.4 White-Rot Fungi

White-rot fungi feed on lignin that gives structure to woody plants (Barr and Aust 1994); thus, decrease in color absorption was observed for two species, namely, *Phanerochaete chrysosporium* and *Tinctoporia* sp., in pulp and paper waste water (Eaton 1980). When used in textile waste water, *Phanerochaete chrysosporium showed* results in 7 days of incubation for removal of dye (Kirby et al. 1997). White-rot fungi produce enzymes such as lignin peroxidase, manganese-dependent peroxidase, glucose-1-oxidase, glucose-2-oxidase, laccase, and phenol oxidase enzyme for removal of dye and lignin degradation in pulp and paper industry and textile industry (Archibald and Roy 1992; Lonergan 1992; Barr and Aust 1994; Thurston 1994; Reddy 1995; Schliephake and Lonergan 1996; Kirby et al. 1997). Dye-containing effluent when treated with *Hirschioporus larincinus*, *Inonotus hispidus*, *Phlebia tremellosa*, and *Coriolus versicolor* (Banat et al. 1996) (Kirby et al. 1997) showed results along with removal of azo dye by *P. chrysosporium* which is not readily degraded by other microorganisms otherwise (Paszczynski and Crawford 1995).

3.7 Combined Treatment Processes

3.7.1 Fenton's Reagent with Microbial Process

Fenton's reagent is used for COD and BOD reduction, as well as odor and color removal. The major drawback of Fenton's reagent is the high demand of H_2O_2 and FeSO4. Temperature, pH, and concentration ratio of both chemical entities are essential parameters affecting its efficiency (Mandal et al. 2010). Fenton's reagent when used with chemolithotrophic microorganism growing on inorganic media with FeSO4 results in advanced oxidation process with the role of microorganism to increase the biodegradability (Tekin et al. 2006). Mandal et al. (2010) studied the effect of the process for COD reduction on industrial effluent comprising of phenolic and organic compound as well as the reduction of the amount of H_2O_2 used in the conventional process without the use of microorganism.

3.7.2 Sulfate-Reducing Bacteria

Sulfide precipitation is done by using sulfate-reducing bacteria. Kousi et al. (2007) developed an upflow fixed-bed SRB to treat zinc-bearing waste water.

3.7.3 Chemical Precipitation with Other Methods

Electro-Fenton process used in combination with chemical precipitation (lime precipitation) for rayon industry waste water showed 88% of COD and 99% zinc removal at a pH range of 9–10 (Ghosh et al. 2011). Papadopoulos et al. (2004) used ion exchange process with chemical precipitation in removal of nickel. Exclusive use of ion exchange process removed up to 75% of nickel and 98% when used in combination with precipitation.

3.8 Drawbacks of Existing Treatments

3.8.1 Microalgae Treatment

Although the treatment technology has many advantages of its own over conventional treatments, the major challenge that comes across is the downstream processing of microalgal suspension and cultivation of microalgae. The presence of **suspended solids** makes it difficult for the light to penetrate, thus resulting in lowered photosynthesis which is necessary for the growth of algae (Larsdotter 2006; Udaiyappan et al. 2017). **Harvesting** of microalgae is tedious as cost and efficiency do not go hand in hand (Lam and Lee 2011).

3.8.2 Oxidative Processes

Flocculation of reagent and dye molecules causes high sludge generation, which requires disposal using Fenton's reagent method (Robinson et al. 2001). The final floc formation and settling quality decide the performance (Raghavachary 1997).

While using ozone for the removal of dye molecules, it was observed that breaking of double bonded dye molecules results in discoloration and formation of smaller molecules. These molecules may be carcinogenic and thus need a simultaneous physical method to overcome it (Peralta-Zamora et al. 1999). The process is cost intensive as the half-life of ozone is as less as 20 min which indicates the requirement of continuous process, making the process expensive (Xu et al. 1999).

The increase in flow rate becomes a problem in dye removal for electrochemical destruction. Though it does not use any chemicals, the cost of electricity being used is equally expensive (Robinson et al. 2001).

3.8.3 Chemical Precipitation

Hydroxide precipitation consumes large amount of chemicals (Jüttner et al. 2000); the sludge produced in the process requires further disposal treatment, and since the sludge has low density, poor settling quality and aggregation make it even more difficult (Yang et al. 2001; Bose et al. 2002; Wingenfelder et al. 2005; Kongsuwan et al. 2009). Many a times the modification in pH is difficult as precipitating pH for all metals is different like in the case of amphoteric metal hydroxides (Fu and Wang 2011).

Sulfide precipitation, when done under acidic condition, can produce H_2S fumes, so non-acidic pH is preferred. Metal sulfide precipitates form colloidal precipitates and become difficult to separate by settling process.

3.8.4 Membrane Filtration

The removal of residue that remains in the filter causing clogging of pores is difficult as it damages the filter if not handled correctly. Membrane cost is the significant expense deciding factor in the process; thus, it cannot be used for effluents heavily loaded by contaminants.

3.9 Conclusion

Over the decades, industrialization has proved to be both boon and bane for mankind. The growing awareness for environment protection has paced up due to the alarming situation that human beings are facing over time. Physicochemical and biological methods for treatment have shown significant results when applied in suitable conditions for various industrial effluents. As already said, Uttar Pradesh is the hub for industries producing multiple forms of effluent. The major pollutants are heavy metals and dyes released by tannery, carpet, and heavy metal industries located in the area. The physical and chemical methods for treating effluents like azo dyes are significant only when the effluent volume is small since the process becomes cost intensive when used in large scale. Biological methods can be useful when cost is considered as they are comparatively cheap, but they are unable to perform under continuous conditions. As fermentation time period cannot be ignored while the effluent is decolorized. Combined process of adsorption followed by solid-state fermentation can yield better results alone in dye decolorization (Nigam et al. 2000). The modern technologies use a combination of biological methods with physical or chemical means to increase efficiency and overcome disadvantages faced when these methods are used individually.

References

Alam MZ et al (2009) Genotoxic and mutagenic potential of agricultural soil irrigated with tannery effluents at Jajmau (Kanpur), India. Arch Environ Contam Toxicol 57(3):463–476

Ali M, Sreekrishnan T (2001) Aquatic toxicity from pulp and paper mill effluents: a review. Adv Environ Res 5(2):175–196

Alloway BJ (2012) Heavy metals in soils: trace metals and metalloids in soils and their bioavailability. Springer, New York

Anderson R (1999) Chromium as an essential nutrient: the chromium file no. 6. International Chromium Development Association, Sheffield

Ansari A et al (2000) Importance of geomorphology and sedimentation processes for metal dispersion in sediments and soils of the ganga plain: identification of geochemical domains. Chem Geol 162(3–4):245–266

Archibald F, Roy B (1992) Production of manganic chelates by laccase from the lignin-degrading fungus Trametes (Coriolus) versicolor. Appl Environ Microbiol 58(5):1496–1499

Ates E et al (1997) Characterization of tannery wastewaters for pretreatment selected case studies. Water Sci Technol 36(2–3):217–223

Bååth E et al (1998) Effect of metal-rich sludge amendments on the soil microbial community. Appl Environ Microbiol 64(1):238–245

Banat IM et al (1996) Microbial decolorization of textile-dyecontaining effluents: a review. Bioresour Technol 58(3):217–227

Barr DP, Aust SD (1994) Mechanisms white rot fungi use to degrade pollutants. Environ Sci Technol 28(2):78A–87A

Baskaran K et al (2003) Wastewater reuse and treatment options for the dairy industry. Water Sci Technol Water Supply 3(3):85–91

Benefield LD, Morgan JM (1990) Chemical precipitation. McGgraw-Hill, Inc., New York, p 1194

Bich NN et al (1999) Combination of Chlorella vulgaris and Eichhornia crassipes for wastewater nitrogen removal. Water Res 33(10):2357–2362

Billings R, DeHaas G (1971) Pollution control in the pulp and paper industry. In: Lund HF (ed) Industrial pollution control book. McGraw-Hill Book Company, New York, pp 18–11

Bose P et al (2002) Critical evaluation of treatment strategies involving adsorption and chelation for wastewater containing copper, zinc and cyanide. Adv Environ Res 7(1):179–195

Britz TJ et al (2006) Treatment of dairy processing wastewaters. In: Waste treatment in the food processing industry. Taylor & Francis, Boca Raton, pp 1–28

Brookes P (1995) The use of microbial parameters in monitoring soil pollution by heavy metals. Biol Fertil Soils 19(4):269–279

Brusick D (1980) Principles of genetic toxicology. Springer, New York

Carvalho F et al (2013) Cheese whey wastewater: characterization and treatment. Sci Total Environ 445:385–396

Cassano A et al (2001) Treatment of aqueous effluents of the leather industry by membrane processes: a review. J Membr Sci 181(1):111–126

Cecen F et al (1992) Biological and advanced treatment of sulfate pulp bleaching effluents. Water Sci Technol 26(1–2):435–444

Chagne V et al (1996) Review of chrome tanning: part 2. Leather 4:77–84

Charerntanyarak L (1999) Heavy metals removal by chemical coagulation and precipitation. Water Sci Technol 39(10–11):135–138

Chen Q et al (2009) Precipitation of heavy metals from wastewater using simulated flue gas: sequent additions of fly ash, lime and carbon dioxide. Water Res 43(10):2605–2614

Chinnasamy S et al (2010) Microalgae cultivation in a wastewater dominated by carpet mill effluents for biofuel applications. Bioresour Technol 101(9):3097–3105

Clarke E, Steinle D (1995) Health and environmental safety aspects of organic colorants. Rev Prog Color Relat Top 25(1):1–5

Courty B et al (2004) Influence of extraction parameters on the mutagenicity of soil samples. Mutat Res Genet Toxicol Environ Mutagen 565(1):23–34

Deepali K, Gangwar K (2010) Metals concentration in textile and tannery effluents, associated soils and ground water. NY Sci J 3(4):82–89

Di Iaconi C et al (2002) Combined chemical and biological degradation of tannery wastewater by a periodic submerged filter (SBBR). Water Res 36(9):2205–2214

Dubey SK et al (2007) Some commercial azo dyes as inhibitors of mushroom tyrosinase DOPA oxidase activity. J Pharmacol Toxicol 2:718–724

Easton M et al (1997) Genetic toxicity of pulp mill effluent on juvenile Chinook salmon (Onchorhynchus tshawytscha) using flow cytometry. Water Sci Technol 35(2–3):347–355

Eaton D (1980) Fungal decolorization of Kraft bleach plant effluents. Tappi 63:103–106

El-Kassas HY, Mohamed LA (2014) Bioremediation of the textile waste effluent by Chlorella vulgaris. Egypt J Aquat Res 40(3):301–308

Field JA et al (1995) Enhanced biodegradation of aromatic pollutants in cocultures of anaerobic and aerobic bacterial consortia. Antonie Van Leeuwenhoek 67(1):47–77

Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: a review. J Environ Manag 92(3):407–418

Ganesh R et al (1994) Fate of azo dyes in sludges. Water Res 28(6):1367–1376

Garbarino J et al (1995) Contaminants in the Mississippi River US Geological survey circular 1133. Virginia USA

Ghosh P et al (2011) Reduction of COD and removal of Zn2+ from rayon industry wastewater by combined electro-Fenton treatment and chemical precipitation. Desalination 266(1–3):213–217

Gowd SS et al (2010) Assessment of heavy metal contamination in soils at Jajmau (Kanpur) and Unnao industrial areas of the ganga plain, Uttar Pradesh, India. J Hazard Mater 174(1–3):113–121

Grismer ME et al (2002) Food-processing wastes. Water Environ Res 74(4):377–384

Gupta S (1980) Some thoughts on standardization of synthetic tanning materials. J Soc Leather Technol Chem 64(1):16–23

Gupta A, Sinha S (2006) Chromium levels in vegetables and grains grown on tannery effluent irrigated area of Jajmau, Kanpur, India: influence on dietary intake. Bull Environ Contam Toxicol 77(5):658–664

Habashi F (1999) Environmental issues in the metallurgical industry progress and problems. REWAS'99: Global Symposium on Recycling, Waste Treatment and Clean Technology

Heidemann E (1993) Fundamentals of leather manufacture. Roether, New York

Horsfall M Jr et al (1999) Speciation of heavy metals in inter-tidal sediments of the Okrika river system, Rivers state Nigeria. Bull Chem Soc Ethiop 13(1):1–10

https://www.ibef.org/exports/leather-industry-india.aspx

Ince N, Gönenç D (1997) Treatability of a textile azo dye by UV/H2O2. Environ Technol 18(2):179–185

Jüttner K et al (2000) Electrochemical approaches to environmental problems in the process industry. Electrochim Acta 45(15–16):2575–2594

Karadag D et al (2015) A review on anaerobic biofilm reactors for the treatment of dairy industry wastewater. Process Biochem 50(2):262–271

Katiyar S (2011) Impact of tannery effluent with special reference to seasonal variation on physicochemical characteristics of river water at Kanpur (UP), India. J Environ Anal Toxicol 1(117):4

Khwaja A et al (2001) Monitoring of ganga water and sediments Vis-a-Vis tannery pollution at Kanpur (India): a case study. Environ Monit Assess 68(1):19–35

Kirby N et al (1997). Bioremediation of textile industry wastewater by white-rot fungi. Stud Environ Sci, Elsevier. 66**:** 711–718

Kongsuwan A et al (2009) Binary component sorption of cu (II) and Pb (II) with activated carbon from Eucalyptus camaldulensis Dehn bark. J Ind Eng Chem 15(4):465–470

Kosolapov D et al (2004) Microbial processes of heavy metal removal from carbon-deficient effluents in constructed wetlands. Eng Life Sci 4(5):403–411

Kousi P et al (2007) A study of the operating parameters of a sulphate-reducing fixed-bed reactor for the treatment of metal-bearing wastewater. Advanced Materials Research, Trans Tech Publications

Kringstad KP, Lindström K (1984) Spent liquors from pulp bleaching. Environ Sci Technol 18(8):236A–248A

Ku Y, Jung I-L (2001) Photocatalytic reduction of Cr (VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide. Water Res 35(1):135–142

Kurniawan TA et al (2006) Physico–chemical treatment techniques for wastewater laden with heavy metals. Chem Eng J 118(1–2):83–98

Kushwaha JP et al (2010) Organics removal from dairy wastewater by electrochemical treatment and residue disposal. Sep Purif Technol 76(2):198–205

Lam MK, Lee KT (2011) Renewable and sustainable bioenergies production from palm oil mill effluent (POME): win–win strategies toward better environmental protection. Biotechnol Adv 29(1):124–141

Larsdotter K (2006) Wastewater treatment with microalgae-a literature review. Vatten 62(1):31

Lenntech K (2004) Water treatment and air purification. Rotter Dam Seweg, Delft

Leyva-Ramos R et al (2005) Adsorption of cadmium (II) from an aqueous solution onto activated carbon cloth. Sep Sci Technol 40(10):2079–2094

Lin SH, Lin CM (1993) Treatment of textile waste effluents by ozonation and chemical coagulation. Water Res 27(12):1743–1748

Lonergan G (1992) White-rot fungi-An environmental panacea? Australas Biotechnol 2(4):214–217

Loprieno N (1982) Mutagenic hazard and genetic risk evaluation on environmental chemical substances. In: Environmental mutagens and carcinogens. University of Tokyo Press Tokyo, Tokyo, pp 259–283

Madhan B et al (2001) Improvements in vegetable tanning-can acrylics be co-tanning agents? J Am Leather Chem Assoc 96(4):120–126

Mandal T et al (2010) Advanced oxidation process and biotreatment: their roles in combined industrial wastewater treatment. Desalination 250(1):87–94

Martin S, Griswold W (2009) Human health effects of heavy metals. Environ Sci Technol Briefs Citiz 15:1–6

Mishra G, Tripathy M (1993) A critical review of the treatments for decolourization of textile effluent. Colourage 40:35–35

Mohan SV, Karthikeyan J (2004) Adsorptive removal of reactive azo dye from an aqueous phase onto charfines and activated carbon. Clean Techn Environ Policy 6(3):196–200

Monser L, Adhoum N (2002) Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater. Sep Purif Technol 26(2–3):137–146

Monteiro CM et al (2009) Characterization of Desmodesmus pleiomorphus isolated from a heavy metal-contaminated site: biosorption of zinc. Biodegradation 20(5):629–641

Montgomery K (1986) Alternatives to chromium tanning-part III: effect of organic acid anions on aluminium sulphate tannage of collagen. J Soc Leather Techn Chem 71:59–67

Nadais, GAG MH, Capela MIAPF, Arroja LMGA, Hung Y-T (2010) Anaerobic treatment of milk processing wastewater. In: Environmental Bioengineering. Humana Press, Totowa, NJ, pp 555–627

Nigam P et al (2000) Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agricultural residues. Bioresour Technol 72(3):219–226

Öğütveren ÜB, Koparal S (1994) Color removal from textile effluents by electrochemical destruction. J Environ Sci Health Part A 29(1):1–16

Oikari A, Nakari T (1982) Kraft pulp mill effluent components cause liver dysfunction in trout. Bull Environ Contam Toxicol 28(3):266–270

Ouki S, Neufeld R (1997) Use of activated carbon for the recovery of chromium from industrial wastewaters. J Chem Technol Biotechnol Int Res Process Environ Clean Technol 70(1):3–8

Özverdi A, Erdem M (2006) Cu2+, Cd2+ and Pb2+ adsorption from aqueous solutions by pyrite and synthetic iron sulphide. J Hazard Mater 137(1):626–632

Pagga U, Taeger K (1994) Development of a method for adsorption of dyestuffs on activated sludge. Water Res 28(5):1051–1057

Pak D, Chang W (1999) Decolorizing dye wastewater with low temperature catalytic oxidation. Water Sci Technol 40(4–5):115–121

Papadopoulos A et al (2004) Nickel uptake from a wastewater stream produced in a metal finishing industry by combination of ion-exchange and precipitation methods. Sep Purif Technol 39(3):181–188

Paszczynski A, Crawford RL (1995) Potential for bioremediation of xenobiotic compounds by the white-rot fungus Phanerochaete chrysosporium. Biotechnol Prog 11(4):368–379

Peck V, Daley R (1994) Toward a “greener” pulp and paper industry. Environ Sci Technol 28(12):524A–527A

Pelegrini R et al (1999) Electrochemically assisted photocatalytic degradation of reactive dyes. Appl Catal B 22(2):83–90

Peplow D (1999) Environmental impacts of mining in eastern Washington. University of Washington Water Center, Seattle

Peralta-Zamora P et al (1999) Degradation of reactive dyes I. a comparative study of ozonation, enzymatic and photochemical processes. Chemosphere 38(4):835–852

Raghavachary C (1997) Colour removal form industrial effluents. A comparative review of available technologies. Chem Eng World 32:53–54

Ramasami T (1999) Beam house and tanning operations: process chemistry revisited. J Soc Leather Tech Chem 83:39–45

Ramos RL et al (2002) Adsorption of zinc (II) from an aqueous solution onto activated carbon. J Hazard Mater 90(1):27–38

Ravi Kumar M et al (1998) Trends in color removal from textile mill effluents. Colourage 45(8):25

Reddy CA (1995) The potential for white-rot fungi in the treatment of pollutants. Curr Opin Biotechnol 6(3):320–328

Robinson T et al (2001) Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresour Technol 77(3):247–255

Rosenwinkel K-H, Austermann-Haun U, Meyer H (2005) Industrial wastewater sources and treatment strategies. Environmental biotechnology: concepts and applications

Sankararamakrishnan N et al (2005) Organochlorine and organophosphorous pesticide residues in ground water and surface waters of Kanpur, Uttar Pradesh, India. Environ Int 31(1):113–120

Saroj S et al (2015) Removal of colour (direct blue 199) from carpet industry wastewater using different biosorbents (maize cob, Citrus Peel and Rice husk). Arab J Sci Eng 40(6):1553–1564

Schliephake K, Lonergan GT (1996) Laccase variation during dye decolourisation in a 200 L packed-bed bioreactor. Biotechnol Lett 18(8):881–886

Serra A et al (1991) Carbonyl compounds in tanning process. AQEIC Boletin Tec 42:24

Shaul G (1987) Fate of azo dyes the activated sludge process. In: Proc. 41st Ind. Waste Conf

Shim J et al (1996) Adsorption of Ni (II), Cu (II), Cr (VI) from multicomponent aqueous solution by pitch-based ACF. Extended abstracts, British Carbon Group

Singh A et al (2012) Continuous metal removal from solution and industrial effluents using Spirogyra biomass-packed column reactor. Water Res 46(3):779–788

Slokar YM, Le Marechal AM (1998) Methods of decoloration of textile wastewaters. Dyes Pigments 37(4):335–356

Spliid NH, Køppen B (1998) Occurrence of pesticides in Danish shallow ground water. Chemosphere 37(7):1307–1316

Star E (2006) US Environmental Protection Agency and US Department of Energy

Tekin H et al (2006) Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater. J Hazard Mater 136(2):258–265

Thompson G et al (2001) The treatment of pulp and paper mill effluent: a review. Bioresour Technol 77(3):275–286

Thurston CF (1994) The structure and function of fungal laccases. Microbiology 140(1):19–26

Trüby P (2003) Impact of heavy metals on forest trees from mining areas. International conference on mining and the environment III. Sudbury, Ontario

Tsachev T (1982) Dairy industry wastewater treatment. In: Industrial wastewater treatment. State Publishing House Technique, Sofia, pp 239–241

Tuxen N et al (2000) Fate of seven pesticides in an aerobic aquifer studied in column experiments. Chemosphere 41(9):1485–1494

Udaiyappan AFM et al (2017) A review of the potentials, challenges and current status of microalgae biomass applications in industrial wastewater treatment. J Water Process Eng 20:8–21

Umbuzeiro G d A et al (2001) The Salmonella mutagenicity assay in a surface water quality monitoring program based on a 20-year survey. Mutat Res Genet Toxicol Environ Mutagen 491(1–2):119–126

United Nations Industrial Development Organization, (UNIDO) (2005) Cost of Tanned Waste Treatment, 15th Session of the Leather and Leather Products Industry Panel Leon, Mexico

Van der Zee FP, Villaverde S (2005) Combined anaerobic–aerobic treatment of azo dyes—a short review of bioreactor studies. Water Res 39(8):1425–1440

Vandevivere PC et al (1998) Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies. J Chem Technol Biotechnol Int Res Process Environ Clean Technol 72(4):289–302

Wang LK et al (2005) Chemical precipitation. In: Physicochemical treatment processes. Springer, Berlin, pp 141–197

Water S, W. H. Organization (2004) Guidelines for drinking-water quality. Vol. 1, recommendations. World Health Organization, Geneva

Wingenfelder U et al (2005) Removal of heavy metals from mine waters by natural zeolites. Environ Sci Technol 39(12):4606–4613

Wojdasiewicz W et al (1992) Tanning with hides to the wet white stages. J Am Leather Chem Assoc 87:121

Xu Y et al (1999) Treatment of textile dye plant effluent by nanofiltration membrane. Sep Sci Technol 34(13):2501–2519

Yadav A et al (2013) Investigation of heavy metal status in soil and vegetables grown in urban area of Allahabad, Uttar Pradesh, India. Int J Sci Res Publ 3(9):1–7

Yang X et al (2001) Removal and recovery of heavy metals from wastewaters by supported liquid membranes. Water Sci Technol 43(2):341–348

Zainal A et al (2012) Phycoremediation in anaerobically digested palm oil mill effluent using cyanobacterium, Spirulina platensis. J Biobaased Mater Bioenergy 6(6):704–709

Zellner G et al (1987) Anaerobic digestion of whey and whey permeate with suspended and immobilized complex and defined consortia. Appl Microbiol Biotechnol 27(3):306–314

Microbial Treatment for Removing Synthetic Dyes from Industrial Effluents

4

Shrabana Sarkar, Priyanka Chakraborty, and Rajib Bandopadhyay

Abstract

Industrial effluent is one of the main causes of environmental pollution. Synthetic azo dyes are widely used in different industries like food, paper, or textile industry. In textile industry, unbound synthetic dyes are released through effluent, which shows awfully sharp effect on the health of different organisms including humans and the entire ecosystem. Though coloured textile industrial effluent has adverse effect on all types of biological network, it has direct effect on water ecosystem because of the general industrial sewage released in nearby water bodies. However, there are different types of physical and chemical waste treatment methods, but those consume huge amount of capital and energy. Microbial processing of waste effluent has capability to trim down drawbacks of chemical methods. In addition, microbial remediation is also environment-friendly and cost-effective. Microorganisms can adapt under any adverse condition due to a huge diversity of enzymes. There are only a few enzymes responsible for dye degradation. Other than that, some common metabolic enzymes may function specially in decolourisation process as well. All these enzymes may be used as beneficial substitute to chemical process. Microbial enzymes are easy to harvest through simple downstream processing and may be easily mobilised. Recent research is going on production of nanoparticle-enzyme conjugate for more efficient remediation of industrial wastes. Until now this research is under laboratory scale, and industrialisation is challenging as well. This chapter deals with detailed information on adverse effect of synthetic dyes, possible microbial process, and future opportunity.

Keywords

Bio-decolourisation · Industrial effluents · Microorganisms · Synthetic dyes

---

S. Sarkar · P. Chakraborty · R. Bandopadhyay (✉)
UGC-Center of Advanced study, Department of Botany, The University of Burdwan,
Burdwan, West Bengal, India

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_4

4.1 Introduction

Water is very essential to live in daily life. Even for industrialisation this is also equally vital. But due to the rapid development and growth of trade, water is getting polluted every day. Azo dye is one of the mostly used pollutants in different industries. It is well known that dyes are readily soluble in water. In many industries, colourants are used efficiently and textile is one of them. Textile manufacturing companies release their coloured waste effluent after dying the fibres in nearby water bodies. This coloured sewage is released without treatment or after some partial treatment most of the time. Azo dyes are very stable coloured compound and unmanageable too (Miran et al. 2015). Due to xenobiotic property of this synthetic dye, those released colourants from textile industry cause lethal diseases that affect microorganisms and macroorganisms of both terrestrial and aquatic ecosystems equally (Krishnamoorthy et al. 2018). Many reports have already been unconfined about the adverse effect of azo dyes to biological system (Krishnamoorthy et al. 2018). Therefore, before releasing the dye-containing water, it needs to be effectively treated to reduce potential risks (Miran et al. 2015).

There are some physical and chemical processes that are already being used by different trades, but those processes fail to remove dyes from water efficiently. Recent trends are going on biological treatment of coloured textile effluent. Microorganisms are ubiquitous in nature and can also live in this unfavourable condition. They can grow in coloured effluent because they use those mixed synthetic and reactive dyes as their main carbon and nitrogen source to continue metabolisms for growth. Many researchers have already been done on these bacteria and tried to use them as efficient environment-friendly technique to clean polluted waters. Azo bonds are hardly eco-friendly to degradation. By sequential treatment with aerobic and anaerobic microorganisms, azo dye can be degraded without formation of carcinogenic aromatic amine, an intermediate. In this type of reaction, aromatic amine is produced in aerophilic condition which is degraded by anaerobic bacteria in the next step of chronological reaction (Lade et al. 2015; Solís et al. 2012; Stolz 2001). Other than this, microbial consortium is being used for eco-friendly degradation of dye-containing effluent (Costa et al. 2018). Even fungus also has the capability of using dye as its nutrient; therefore, it degrades the dye-containing sludge.

Bacteria and fungi produce some kind of special enzymes, namely, laccase and azoreductase, which have the ability to break down the carcinogenic azo bond potentially (Singh et al. 2015; Kalyani et al. 2012; Russ et al. 2000; Verma et al. 2019). An enzyme has a catalytic activity that increases the rate of reaction. It is used in very minute concentration. Due to the presence of this unique characteristic, immobilised enzymes and enzyme-mediated nanoparticles are also being used as recent trend for fast and proficient dye degradation practice (Sha et al. 2016). Though these processes have already achieved their success in laboratory scale, this practice is still a challenge when used economically at industry level (Zhang et al. 2018). Ongoing research will establish those processes in industry level in the near future. This chapter has discussed possible environment-friendly techniques including recent trends of research elaborately, which will open future paradigm on this field to keep the environment fresh.

4.2 Chemistry of Synthetic Dye

Synthetic dyes are generally made either from petroleum by-products or from earth minerals. In the story of preparation of azo compound coupling reaction between diazonium compound and naphthol, pyrazole phenol is the very important part. This coupling reaction in optimum pH and temperature causes the formation of the perfect colour of azo dyes. After the reaction has been completed, dye stuffs have been salted out as suspension (Allen 1971). This dye forms colour due the presence of chromophore group in its chemical structure. Tautomeric equivalent of some compounds like aminoazo or hydroxyazo is required for the formation of chromophore group of azo dye (Allen 1971). Many substantive dyes which bind to fibres are manufactured from intermediates of other fundamental dyes (Allen 1971). Synthetic azo dyes, one of the mostly used synthetic dyes, are coloured substance that readily gets mixed in aqueous solution for its great affinity to water.

Azo dyes are named so because of the presence of –N=N- group in its chemistry (Madkour et al. 2016; Sudha et al. 2014; Barragán et al. 2007). This special bond creates stereoisomerism which is responsible for trans and cis format of side linkages with the bond (Allen 1971). The planarity (Π) of the molecule and lone pair electron of nitrogen atom is a vital part of chemical construction to find out the absorption property. Presence of this group boosts the assimilation capacity and deterioration inhibition efficiency (Madkour et al. 2016). Hence, the azo bond is responsible for perilous effect on the environment. Generally azo dyes contain one, two, or more azo linkages based on which they are of different classes, such as mono-azo dye, di-azo dye, and tri-azo dye (Fig. 4.1). Other than that, dye structure also may contains sulphonic group (SO^{3-}) for huge commercial interest (Sudha et al. 2014; Barragán et al. 2007), naphthyl ring, linking phenyl in addition to other functional groups like sulphonate, hydroxyl, triazine amine, methyl, chloro, etc. (Bell et al. 2000). Inhibition effect is also sometime determined by the presence of types of functional groups in addition to its physical and chemical characteristics and electronic density (Madkour et al. 2016). Other than these, there are various types of detrimental dyes such as metal complex, acidic dye, basic dye, direct, mordant, and reactive dyes, of which reactive dyes are widely used in the textile industry (Lucas and Peres 2006). Based on affinity toward the water molecules, dyes are of two types: one is hydrophobic and another is hydrophilic. Hydrophobic azo dye can be easily taken up by microorganisms and reduced within the cell, but the hydrophilic azo dyes get reduced outside the cell.

4.3 Hazardous Effect of Synthetic Dyes on Ecosystem

Dye is an essential part of many industries like textile, leather, paper, food, and many more (Kanagaraj et al. 2015). Mainly synthetic azo dyes are used in industry since 2000 BC as an integral socioeconomic part. This is one of the main causes of industrial revolution. Azo dyes are the largest group of chemically synthesised dye used in industry. In azo bond (-N=N-), nitrogen is an electron withdrawing group (Solís et al. 2012). Due to presence of this chemical feature, azo dyes are not only

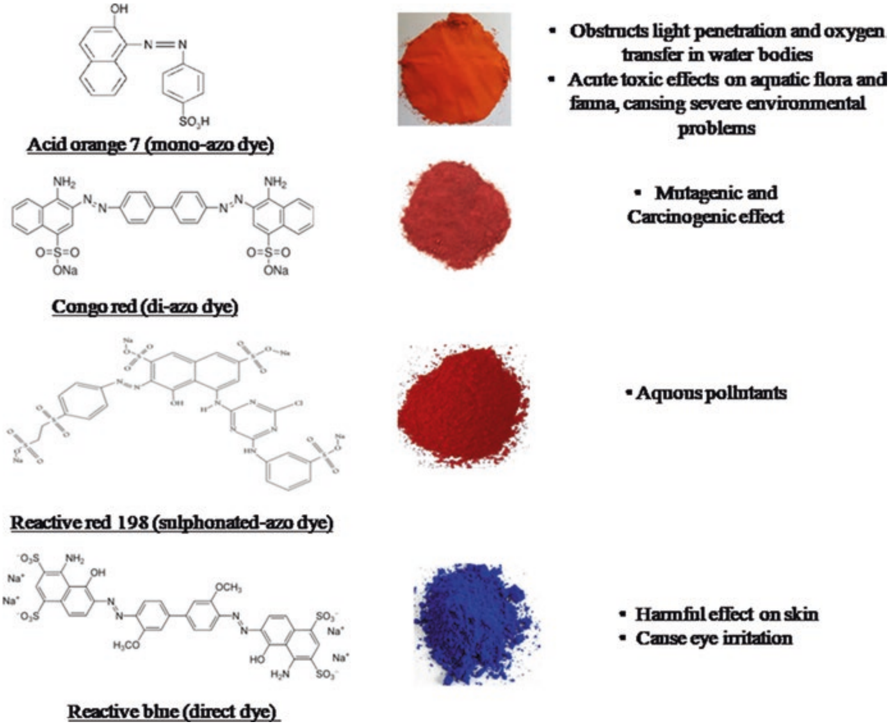


Fig. 4.1 Chemical structure of different synthetic azo dyes

less susceptible but also highly cancerous and insubordinate in nature (Kanagaraj et al. 2015). Due to this resistance to degradation nature, it can sustain for a long time in the soil (Krishnamoorthy et al. 2018). For this reason, the fertility of the soil also gets reduced abruptly. Different azo dyes are used in the textile industry in their commercial name, of which 10–15% is released through waste water either without any treatment or with partial treatment (Sarkar et al. 2017). Due to rapid industrialisation, use of azo dyes increases day by day and so the rate of pollution. This released coloured industrial effluent is the main reason behind the toxicity and mutagenicity of living organisms in the ecosystem. It is also responsible for disturbing the ecological niche (Kurade et al. 2019). Due to inadequate treatment of dyes, they remain in the environment for a long time and exhibit their xenobiotic properties badly (Carmen and Daniela 2012).

One of the main industries is textile where synthetic azo dyes are used widely. Normally unbound dyes, which fail to bind with fibers in textile industry are released in the nearby water bodies. These dyes are the main cause behind increasing biological oxygen demand (BOD), pH, and chemical oxygen demand (COD) of those water bodies (Sen et al. 2016; Solís et al. 2012). Aquatic fauna and flora get affected badly by the change of haematological parameters. This is also a threat to the water ecosystem through food chain (Fathima et al. 2019) and causes misbalance of organic and inorganic contents of water bodies. Amalgamation of dye-containing sludge in the water reduces light penetration which arrests photosynthesis of hydrobionts (Hernández-Zamora and Martínez-Jerónimo 2019). Actually high accumulation of benzene-based azo dye in photosynthetic plants' body inhibits photosynthetic pigment to do reaction. As all ecosystems in the biosphere are interrelated with each other, not only the water ecosystem but also all other ecosystems are affected. Toxic azo dyes normally accumulate in the bodies of fishes and other aquatic animals which are further taken up by humans, causing sporadic disorder, hypertension, cancer related to mutation, and many other deadly diseases (Kanagaraj et al. 2015). According to the National Institute for Occupational Safety and Health database, benzene-based azo dye, viz. Congo red (Hernández-Zamora and Martínez-Jerónimo 2019), shows carcinogenic effect on individual's urinary bladder and different nuclear incongruity in the animals used for laboratory examination (Sudha et al. 2014). Even Congo red exposure causes harsh damage in the heart by reducing the heartbeat and deformities in the skeleton and embryos of Zebra fishes (Fig. 4.2). Hatching of many fish larvae is inhibited by the contamination with azo dyes (Hernández-Zamora and Martínez-Jerónimo 2019). Aside from Congo red, many other synthetic azo dyes like Acid Violet 7 and malachite green are the key reason for lethal chromosomal aberration in cells (Mansour et al. 2010; Puvaneswari et al. 2006; Srivastava et al. 2004). One of the histopathological effects of malachite green is multi-organ tissue injury (Srivastava et al. 2004). One of the key characteristics of azo dye is immediate solubility with water. Therefore, it is easy for the skin to absorb and increases the risk of irritation, allergy, and skin cancer (Sudha et al. 2014). Reactive brilliant red is regularly used in textile due to its fast fixation ability, but by rapid absorption, it has a lethal effect on serum albumin, protein, and enzymes by altering their function (Li et al. 2010). Therefore, commercially used synthetic

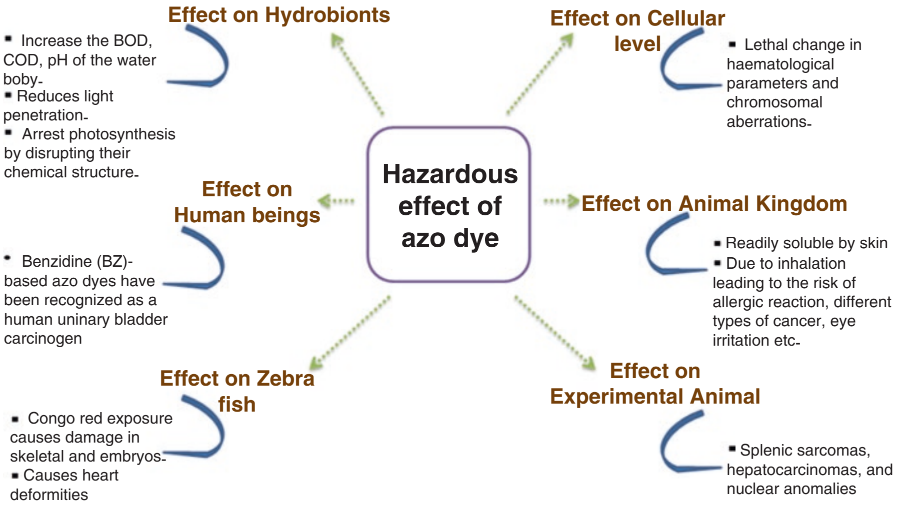


Fig. 4.2 Diagrammatic representation of the hazardous effect of azo dye on biosphere

azo dyes are promising contaminants reported to have an adverse effect to the living world (Fig. 4.2).

4.4 Available Physicochemical Methods for Industrial Effluent Remediation

Physical and chemical methods were used in industries in the 1920s for degradation of coloured effluents. Those available processes were very costly, produce secondary pollutant, and were not able to degrade azo dye-containing waste water effectively. Mostly available processes are flocculation, adsorption, oxidation, ion exchange, activated carbon adsorption, ozonation, Fenton process, electrochemical process, etc. (Singh et al. 2015; Lade et al. 2015). Among all these, adsorption is thought to be the most effective one. In this process, organic dyes are adsorbed on a solid phase in order to separate it from the water part. Activated carbon process was popular in textile. Though it had great decolourisation efficiency, cost-insensitive regeneration is the main constraint of this process. Another popular process for dye degradation is Fenton process which has great efficacy without alteration of volume but is prohibitively high-priced. Hence, industry doesn't feel free to use this process for processing their waste water. Ozonation is another process exclusively used for azo dye removal, but it produces amine as secondary pollutant. Amine is very dangerous being a xenobiotic component (Anjaneyulu et al. 2005).

Available physical and chemical process has been advanced for increasing the efficacy of degradation. For example, advanced oxidation process is used in tannery and textile industry for waste effluent remediation, but it is a cost-intensive procedure (Anjaneyulu et al. 2005). Research and review on these methods have proved that all procedures are either enormously expensive or produce secondary pollutants. None of them are exclusively effective without any side effect. For these reasons, microorganism-mediated degradation of dye-containing textile waste effluents comes into account and becomes increasingly popular within a very short period because of its efficiency and zero side effects on environment.

4.5 Microorganism-Mediated Degradation of Coloured Industrial Effluents

Previously discussed physical and chemical processes are used in some industries but not efficient for complete degradation followed by production of non-toxic compound at the completion of the reaction. Available processes are much costly and produce sludges followed by the production of secondary pollution (Mani and Hameed 2019). Microorganisms are capable of producing non-carcinogenic end products after degradation. Because of their quick and easy adaptability capacity, microorganisms can live under any unfavourable condition. It also has been found that both fungi and bacteria can mineralise and decolourise textile dye-containing sludge potentially (Chacko and Subramaniam 2011). It is already known than dye-containing waste water shows a very high COD value which is not acceptable to use for mankind. Microorganism-mediated cleaning of coloured effluent shows great reduction of COD value (Cao et al. 2018), which can be used for later treatment and for primary washing in textile manufacturing companies or in agricultural fields. The bacteria which have the ability to degrade the dye have some special characteristics like elevated production of biomass and aggressive growth (Kurade et al. 2019). Microbial cultures use a mixture of dyes as intermediates of their metabolic pathway. The reason behind this intense biodegradation is concentrated catalytic activity, although the pH and temperature are unfavourable for the growth of any other living organisms (Kurade et al. 2019). Even mixed fungal culture shows great ability in using intermediates produced after degradation of azo dyes as their source of nutrient and modifies them into a non-toxic component (Krishnamoorthy et al. 2018).

In recent era of fast industrialisation, use of phenol and polycyclic aromatic hydrocarbon-containing dyes, which are a petroleum by-product, has been increased significantly. To save the environment, it is needed to release eco-friendly materials after treatment of industrial waste, and previously maintained dyes are not atmosphere friendly at all. After degradation, environment-friendly materials can also be used for the purpose of land filling (Singh and Kumar 2019). This will not harm the organic and mineral composition of that land. Including this, it will not cause any severe destruction of soil ecosystem too. As per previous discussion, it is found that regular decolourisation process produces aromatic amine which is the widespread reason of pollution (Singh and Kumar 2019). Microorganisms have the capacity to reduce the amount of this pollutant significantly. In the following parts, names of microorganisms and their mechanisms in the treatment of dye-containing waste have been discussed.

4.5.1 Fungi in Degrading Coloured Industrial Effluent

Fungus has potential to degrade industrial waste water containing azo dyes. Mycoremediation causes significant reduction of BOD and COD, nearly 60% or more than that sometimes (Ortiz-Monsalve et al. 2019). Nearly 70% detoxification has also been reported after fungal biodegradation of azo dye-containing waste water. There are different types of fungi which show bioremediation property of different level. As per example, white-rot fungi had shown great potential in dye degradation because of their high bioaccumulation and biosorption property (Ortiz-Monsalve et al. 2019). As per previous discussion, dyes are used in different industries, like textile dyeing and leather tanning, and type of waste and chemical composition are different. Based on that data, it has been found that fungi are mainly used to degrade leather waste than textile effluent. *Trametes villosa* SCS-10 has shown decolourisation capacity up to 90% for three dyes used in leather industry like Acid Blue 161, Acid Red 357, and Acid Black 210 (Table 4.1). This experiment has proven outstanding biosorption property of fungi because of the presence of laccase, a special dye degrading enzyme (Ortiz-Monsalve et al. 2017).

Table 4.1 List of currently used fungal strains responsible for degradation of azo dye

Name of fungus	Dyes degraded by organisms	References
Aspergillus flavus	Different azo dyes	Eslami et al. (2019)
Trichoderma sp.	Malachite green	Mani and Hameed (2019)
Pycnoporus sanguineus	Anthraquinone dye Remazol Brilliant Blue R	Rodríguez-Couto (2019)
Trametes villosa SCS-10	Acid Orange 142 and Acid Red 357	Ortiz-Monsalve et al. (2019)
Trametes versicolor	Direct Blue, Direct Red 128	Tochhawng et al. (2019)
Trametes pubescens	Textile dye	Rekik et al. (2019)
Dichotomomyces cejpii MRCH 1-2 and *Phoma tropica MRCH*	Congo red	Krishnamoorthy et al. (2018)
Pseudoglarobasidium acaciicola	Poly R	Barathikannan et al. (2017)
Trametes trogii	Reactive Black 5 (diazoic) and Reactive Violet 5	Sayahi et al. (2016)
Marasmius sp. BBKAV79	Textile industrial dyes	Vantamuri and Kaliwal (2016)

The dye degrading capability of fungus is due to the presence of a special enzyme, laccase (Rodríguez-Couto 2019). There are many fungi like *Saccharomyces cerevisiae* and two basidiomycota like *Trametes versicolor* and *T. trogii* which have optimised dye degradation capacity due to presence of special enzymes. By using minimal growth medium, fungus can degrade textile dyes from industrial waste (Antošová et al. 2018). Other than basidiomycetes, some endophytic fungi also exhibit decolourisation capacity against a wide range of azo dyes like Congo red, crystal violet, methyl orange, and methyl red, released from paper, leather, or textile industry (Tochhawng et al. 2019). This is eco-friendly and trims down toxicity. Endophytic fungus, which mainly resides in plant tissues, produces laccase as extracellular enzyme. This enzyme is responsible for decolourising capacity. It has been reported that fungi that have dye decolourising capacity also exhibit ligninolytic potential (Joseph et al. 2019). Not only single fungi but also fungal consortia have been reported to degrade azo dye efficiently (Krishnamoorthy et al. 2018). From previous report, it has been found that basidiomycetes have more potential to decolourise dye-containing industrial effluent than other classes (Munir et al. 2017). Thus, this is very important to understand the clear mechanism behind degradation.

4.5.2 Bacteria in Processing Industrial Sludge

Endeavour of recognising the bacteria that have the ability to degrade the azo dye started in 1970. At that time, primarily isolated three strains were *Bacillus subtilis*, *Aeromonas hydrophila*, and *Bacillus cereus* (Dave et al. 2015; Wuhrmann et al. 1980). There are a number of bacteria which have the ability to reduce azo dyes non-specifically. Lots of bacteria for degradation of synthetic and reactive commercial dyes, viz. *Pseudomonas* sp., *Bacillus subtilis* (Kannan et al. 2019), *Geobacillus* sp., *Rhabdobacter* sp., *Escherichia coli*, *Enterococcus* sp., *Staphylococcus* sp., *Corynebacterium* sp., *Rhizobium* sp., *Lactobacillus* sp., *Xenophilus* sp., *Clostridium* sp., *Acinetobacter* sp., *Dermacoccus* sp., *Micrococcus* sp., *Proteus* sp., *Morganella* sp., *Aeromonas* sp., *Alcaligenes* sp., *Shewanella* sp., *Klebsiella* sp., *Alishewanella* sp., etc., have been widely reported for consequential biodegradation of azo dyes (Imran et al. 2016; Kolekar et al. 2013; Haghshenas et al. 2016; Sudha et al. 2014). This report proves the versatile nature of bacteria.

Azo dyes are highly photolytically stable which makes them more resistant to degradation (Ayed et al. 2017). Bacteria or their consortia have potential to degrade azo dye singly or by synergistic reaction (Table 4.2). There are broadly two types of degradation: **(a)** by single strain and **(b)** by a mixture of two or more strains (consortia). *Planococcus* sp. is a novel strain that has shown nearly 80% degradation to Orange 3K, after setting all parameters of reaction in optimum scale (Chanwala et al. 2019). It is reported from recent research that *Enterococcus faecalis–Klebsiella variicola* consortia have the ability to degrade Reactive Red 198 more than 99% by three days incubation (Eslami et al. 2019). Other than these two broad categories, immobilised enzymes, activated sludge, enzyme-mediated nano-conjugates, and bioreactors are the part of present time. Microbes are part of the environment, so microbial degradation is an eco-friendly and cost-effective technique. Besides this, biological treatment is a stabilised process and removes the carcinogenic effect of azo dyes. Bioremediation can be done by different processes like anaerobic culture, activated sludge, bioaugmentation, etc. (Karpagam et al. 2019). According to recent research, it has been found that bacterial cell concentration is a big factor including other parameters (Eslami et al. 2019). Different supplementary nutrition also increases the rate of degradation significantly. In order to understand the clear growth pattern of bacterial strains, their enzymes need to be studied.

4.5.3 Enzymatic Degradation of Coloured Waste

All microbial degradation is possible due to the presence of some special kinds of enzymes which are produced mainly in extracellular fashion but sometimes in intracellularly too. There are mainly two types of enzymes, namely, laccase and azoreductase (Singh et al. 2015). Other than this, sometimes under adverse condition, oxidase and peroxidase also act as dye degrading enzymes (Santos et al. 2014). These enzymes may be found from another sources including plant other than microbes. Enzymes have broad range of substrate specificity and work in high efficacy. As enzyme catalyses only the required reaction and is cost-effective, trouble-free to immobilise, and a product of biological organisms, it causes negligible ecological pollution. The only factor that needs to be taken under consideration is temperature, because enzymes are proteinaceous in nature. Protein is normally

Table 4.2 List of presently used bacterial strains responsible for degradation of azo dye

Name of the bacteria	Name of azo dye degraded by bacteria	References
Bacillus sp. strain AK1, *Lysinibacillus* sp. strain AK2 *Kerstersia* sp. strain VKY1 and consortia	Ponceau 4R	Masarbo et al. (2019)
Enterococcus faecalis–Klebsiella variicola	Reactive Red 198	Eslami et al. (2019)
Bacillus sp.	Orange 3K	Chanwala et al. (2019)
C. acidovorans, *Bacillus cepacia*	Direct Blue 75, acid orange 7	Chanwala et al. (2019)
Bacillus sp. and *Micrococcus* sp.	Congo red and alizarin red	Ito et al. (2018)
Bacillus subtilis and *Micrococcus luteus*	Anthraquinone dyes	Ito et al. (2018)
Bacillus farraginis	Orange M2R	Siddique and Alif (2018)
Paenibacillus macerans	Green GS	Siddique and Alif (2018)
Staphylococcus aureus	Reactive Violet 5	Ayed et al. (2017)
Bacillus sp. strain CH12	Reactive Red 239	Guadie et al. (2017)
Shewanella spp.	Reactive Black 5, Direct Red 81, Acid Red 88, Acid Yellow, Orange 3. Reactive blue	Imran et al. (2016)
Geobacillus stearothermophilus	Indigo carmine	Mehta et al. (2016)
Aeromonas hydrophila	Malachite green, brilliant green, crystal violet	Mahmood et al. (2016)
Escherichia coli JM 109	Direct Red 71	Mahmood et al. (2016)
Lysinibacillus sp. AK2	Metanil yellow (sulfonated azo dye)	Mahmood et al. (2016)
Pseudomonas entomophila BS1	Reactive Black 5	Khan and Abdul (2015)
Micrococcus luteus	Acid Black	Kanagaraj et al. (2015)
Aeromonas sp. DH-6	Methyl Orange	Du et al. (2015)
Bacillus spp.	Acid Red 119, Navy Blue 2GL, Acid Orange 10	Dave et al. (2015)
Pseudomonas spp.	Reactive Black, Reactive Blue, Orange I and II	Dave et al. (2015), Lade et al. (2015), and Khan and Abdul (2015)

thermo-liable. Recently, this problem has been alliviated by isolating thermostable enzymes from heat-tolerable microorganisms. Other than this, the by-products, produced from enzymatic reactions, can be used as additional supply for media intended for microbial culture and growth.

Use of laccase of microbial origin in degradation of azo dye-containing effluent started long year back in the 1990s (Wong and Yu 1999). From phylogenetic story, it is revealed that the enzyme evolved from small prokaryotic protein, namely, azurin (Singh et al. 2015). Laccase is a multi-copper oxidase enzyme which has a wide range of applications in the field of biotechnology including coloured effluent treatment in an environment-friendly way. Though in majority laccase is being isolated from fungus, as, for example, white-rot fungus, it can also be isolated from bacteria. There is one disadvantage of fungal laccase, i.e. it cannot withstand high temperature and high pH condition, which is very common for industrial reaction (Singh et al. 2015). This special enzyme isolated from microorganisms is reported for its extensive capacity in azo dye degradation. This enzyme has non-specific oxidation capacity which is important for bioremediation process. On the other hand, laccase does not require any cofactor or oxygen for reaction (Singh et al. 2015). Mainly dye molecule with low molecular weight is being used as redox mediator in the process of decolourisation. Aromatic azo dyes, phenolic compound, etc. are degraded by laccase. Now, pH-stable and thermo-stable laccase are being isolated which also exhibit tolerance to organic solvent (Guan et al. 2014). In the path of reaction, laccase uses Cu^{2+} as a mediator to oxidise aromatic amine.

Azoreductase is a catalytic enzyme and it name so because of the presence of property to break azo bond. In reaction, azoreductase degrades azo bond and produces colourless aromatic amine. Azoreductase is an intercellular or membrane-bound enzyme. It sometime can easily diffuse and bind to a membrane where it breaks azo bond. Mechanism of membrane-bound azoreductase is known, but due to positional complexity, machinery of the cytoplasmic one is unknown. Sulphonated azo dye is efficiently degraded by cytoplasmic azoreductase (Chacko and Subramaniam, 2011). Unlike laccase, azoreductase has substrate specificity and efficiency in dye degradation. The enzyme breaks –N=N- bond by oxidising the substrate (Fig. 4.3). For this reaction, it transfers four electrons to azo bond as reducing equal to break double bond. This reaction occurs in two steps in each, of which two electrons are transferred (Sarkar et al. 2017). Toxic aromatic amine is produced as a toxic and xenobiotic intermediate which can be cleaned out by aerobic bacteria (Singh et al. 2015). As laccase uses Cu^{2+} as reaction mediator, azoreductase uses NADH or FADH2 as reaction mediator.

It is already has been taken into account that under adverse condition, some regular microbial enzyme can act as dye degrading enzyme, for example, flavin reductase of *E. coli* (Russ et al. 2000) which uses FDH_2, peroxidase of bacteria (Santos et al. 2014), and manganese peroxidase of fungi (Rekik et al. 2019). Peroxidase has normally oxidative catalytic activity on H_2O_2, but under adverse condition, this haemoprotein degrades azo dye efficiently. Besides decolourisation, peroxidase has another important role in detoxification. Majority of sulphonated and phenylalanine-containing dyes are foremost substrates of this enzyme. Fungal peroxidase can degrade anthraquinone type of azo dye. Due to higher Km value, manganese peroxidase prefers ortho methyl group in meta position of chromophore group in chemistry of azo dye.

All these enzymes are already isolated majorly from microorganisms in the laboratory. Their application in dye degradation also has been checked. Enzyme is used in minute condition and can be recycled sometimes. It also increase the rate of

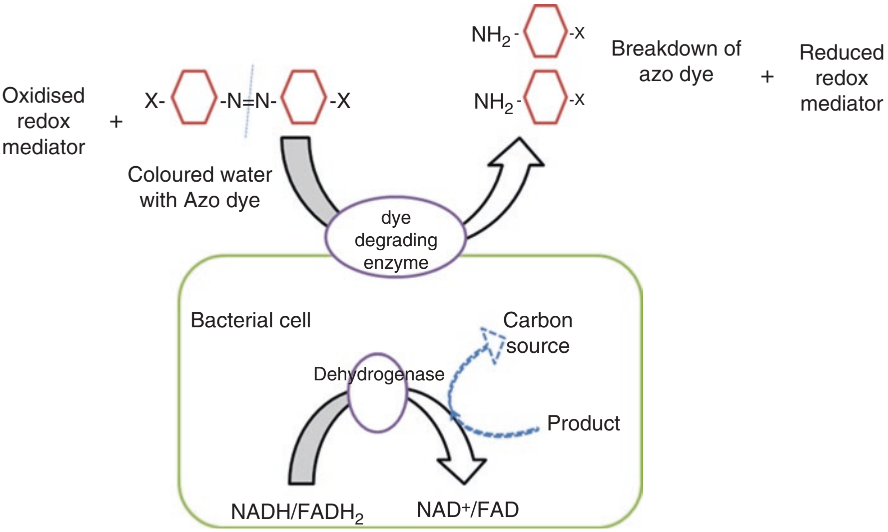


Fig. 4.3 Diagrammatic representation of mechanism behind enzymatic breakage of azo bond and its use as carbon source

reaction and most importantly it is an environment friendly process. Therefore, out of the laboratory in pilot scale bioremediation, enzymes are being expected to be used extensively. Though much research has already been done, it is long way to reach in industry. As we have already discussed, biological treatment is more welcome than physio-biochemical treatment to keep the environment green and pollution-free.

4.6 Research Trends on Microbial Treatment of Dye-Containing Waste Materials

Previously chemical or physical process was being used in order to decolourise dye-containing effluent. Later, day-by-day microbial technique has come into account for this purpose. Single bacteria are being used in order to degrade azo dyes efficiently. To get more effective result, researchers have used consortia, i.e. mixture of two or more bacteria, for degradation purpose. Synergistic action of two or more microorganisms shows better degradation capacity than single organism (Eslami et al. 2019; Masarbo et al. 2019). Other than this, fungal–bacterial consortia are also reported for their superior role in bioaccumulation (Mani and Hameed, 2019). Many studies had been done in order to understand the reason behind microbial degradation. Researchers found enzyme as the cause of degradation. We all know that enzyme acts as catalyst of a reaction. By using very minute concentration, it shows great potential to increase reaction rate significantly. Therefore, instead of using bacterial cell, direct isolated enzymes have been used for degradation of azo dye. By this reaction, efficiency increases significantly (Chacko and Subramaniam 2011; Singh et al. 2015).

Microbial fuel cell is another more advanced method designed for degradation purpose (Wang et al. 2019). Based on mechanism of sequential aerobic and anaerobic treatment by bacteria, microbial fuel cell has been designed. More advanced mechanisms increase the degradation rate and decrease the time spent for the treatment. Recent researchers are focusing more on an eco-friendly and cheaper technique in order to reduce environmental pollution. Palladium is used as an effective cofactor for increasing the rate of degradation reaction. Therefore, palladium is being used in reaction for increasing degradation potentiality (Mohammad-Salehi et al. 2019). Other than this, use of immobilised dye degrading special enzyme with graphene nano-materials in recent years shows increased folds of degradation potentiality (Kashefi et al. 2019). In the near future, it is being planned to use microorganism-mediated nanoparticle for degradation of azo dye-containing coloured effluents.

4.7 Conclusion

In industrial effluent, not only azo dye or other specific organic or inorganic chemicals are present, rather, this is a very complex type of waste due to the presence of different traces of synthetic toxic chemicals. Therefore, this is the main cause of severe environmental pollution. Available physical and chemical methods are very expensive and produce secondary pollutant, aromatic amine which is carcinogenic. Microbial degradation is effective and produces no other pollutants as reaction products. Consortia made up of aerobic and anaerobic bacteria or fungal–bacterial instead of one single microorganism are more effectual for degradation of dye-containing waste. A large variety special enzymes have been isolated from microorganisms which attack complex dye material for faster degradation.

Recent trends on degradation of azo dyes observe an idea shift by invention of nano-conjugates. Enzyme nanoparticles make remediation reaction more substrate specific and more efficient. After nanoparticle formation due to increased surface area, remediation efficacy increases several folds. Chemically stable cobalt nanoparticles have shown immense potential to degradation (Sha et al. 2016). Titanium nano-conjugate has been formed with immobilised fungal laccase which shows increased efficiency towards coloured effluent degradation. Enzymatic nanoparticle mediated process is able to degrade dye within a very short period of time in a critical temperature and pH. Thus, advanced modification on enzymatic degradation is considered as the most outstanding weapon for microorganism-mediated degradation to fight against the toxic effect of dye or chemical–physical dye degrading process. As it is inexpensive and environment friendly with zero secondary pollutant production, it exhibits momentous potential to degradation.

References

Allen RLM (1971) The chemistry of azo dyes. In: Colour chemistry, Studies in modern chemistry. Springer, Boston

Anjaneyulu Y, Chary NS, Raj DSS (2005) Decolourization of industrial effluents–available methods and emerging technologies–a review. Rev Environ Sci Biotechnol 4(4):245–273

Antošová Z, Herkommerová K, Pichová I, Sychrová H (2018) Efficient secretion of three fungal laccases from Saccharomyces cerevisiae and their potential for decolorization of textile industry effluent—a comparative study. Biotechnol Prog 34(1):69–80

Ayed L, Bekir K, Achour S, Cheref A, Bakhrouf A (2017) Exploring bioaugmentation strategies for azo dye CI reactive violet 5 decolourization using bacterial mixture: dye response surface methodology. Water Environ J 31(1):80–89

Barathikannan K, Ramasamy KP, Manohar CS, Meena RM (2017) Diversity and decolorization potential of fungi isolated from the coral reef regions off Kavaratti, India. Indian J Geo-Mar Sci 46:497–503

Barragán BE, Costa C, Márquez MC (2007) Biodegradation of azo dyes by bacteria inoculated on solid media. Dyes Pigments 75(1):73–81

Bell J, Plumb JJ, Buckley CA, Stuckey DC (2000) Treatment and decolorization of dyes in an anaerobic baffled reactor. J Environ Eng 126(11):1026–1032

Cao X, Wang H, Zhang S, Nishimura O, Li X (2018) Azo dye degradation pathway and bacterial community structure in biofilm electrode reactors. Chemosphere 208:219–225

Carmen Z, Daniela S (2012) Textile organic dyes–characteristics, polluting effects and separation/elimination procedures from industrial effluents–a critical overview. In: In Tech (ed) Croatia organic pollutants ten years after the Stockholm convention-environmental and analytical update. Intech, Rijeka, pp 55–81

Chacko JT, Subramaniam K (2011) Enzymatic degradation of azo dyes-a review. Int J Environ Sci 1(6):1250

Chanwala J, Kaushik G, Dar MA, Upadhyay S, Agrawal A (2019) Process optimization and enhanced decolorization of textile effluent by *Planococcus* sp. isolated from textile sludge. Environ Technol Innov 13:122–129

Costa AFS, Albuquerque CDC, Salgueiro AA, Sarubbo LA (2018) Color removal from industrial dyeing and laundry effluent by microbial consortium and coagulant agents. Process Saf Environ Prot 118:203–210

Dave SR, Patel TL, Tipre DR (2015) Bacterial degradation of Azo dye containing wastes. Microbial degradation of synthetic dyes in wastewaters. Springer, Cham, pp 57–83

Du LN, Li G, Zhao YH, Xu HK, Wang Y, Zhou Y, Wang L (2015) Efficient metabolism of the azo dye methyl orange by *Aeromonas* sp. strain DH-6: characteristics and partial mechanism. Int Biodeterior Biodegradation 105:66–72

Eslami H, Shariatifar A, Rafiee E, Shiranian M, Salehi F, Hosseini SS, Ebrahimi AA (2019) Decolorization and biodegradation of reactive Red 198 Azo dye by a new *Enterococcus faecalis–Klebsiella variicola* bacterial consortium isolated from textile wastewater sludge. World J Microbiol Biotechnol 35(3):38

Fathima PS, Priyatha CV, Chitra KC (2019) Ameliorating effect of vitamin C on acid Orange 7 induced oxidative stress in the gill of the fish, *Anabas testudineus* (Bloch, 1792). Res Rev J Toxicol 8(3):15–27

Guadie A, Tizazu S, Melese M, Guo W, Ngo HH, Xia S (2017) Biodecolorization of textile azo dye using *Bacillus* sp. strain CH12 isolated from alkaline lake. Biotechnol Rep 15:92–100

Guan ZB, Song CM, Zhang N et al (2014) Overexpression, characterization, and dye-decolorizing ability of a thermostable, pH-stable, and organic solvent-tolerant laccase from *Bacillus pumilus* W3. J Mol Catal B Enzym 101:1–6

Haghshenas H, Kay M, Dehghanian F, Tavakol H (2016) Molecular dynamics study of biodegradation of azo dyes via their interactions with AzrC azoreductase. J Biomol Struct Dyn 34(3):453–462

Hernández-Zamora M, Martínez-Jerónimo F (2019) Exposure to the azo dye direct blue 15 produces toxic effects on microalgae, cladocerans, and zebrafish embryos. Ecotoxicology 1–13

Imran M, Negm F, Hussain S, Ashraf M, Ashraf M, Ahmad Z, Arshad M, Crowley DE (2016) Characterization and purification of membrane-bound Azoreductase from Azo dye degrading *Shewanella* sp. strain IFN4. CLEAN Soil Air Water 44(11):1523–1530

Ito T, Shimada Y, Suto T (2018) Potential use of bacteria collected from human hands for textile dye decolorization. Water Res Ind 20:46–53

Joseph JT, Mahalakshmia R, Revathy K, Panneerselvam K, Manikandan P, Shobana CS (2019) Effectiveness of application of lignolytic fungal strains, *Cladosporium uredinicola* GRDBF21 and *Bipolaris maydis* GRDBF23 in the treatment of tannery effluent. J Environ Biol 40(2):158–164

Kalyani DC, Telke AA, Surwase SN, Jadhav SB, Lee JK, Jadhav JP (2012) Effectual decolorization and detoxification of triphenylmethane dye malachite green (MG) by Pseudomonas aeruginosa NCIM 2074 and its enzyme system. Clean Techn Environ Policy 14(5):989–1001

Kanagaraj J, Senthilvelan T, Panda RC (2015) Degradation of azo dyes by laccase: biological method to reduce pollution load in dye wastewater. Clean Techn Environ Policy 17(6):1443–1456

Kannan D, Devi R, Murugesan AG, Rajan S (2019) Studies on decolorization of textile dye by using Pseudomonas and bacillus sp from the contaminated effluent soil samples of Kovilpatti, Thoothukudi district of Tamil Nadu. J Appl Nat Sci 11(1):134–137

Karpagam P, Manikandan R, Selvakumar S (2019) Decolorization and bioremediation of textile dye effluent by bioreactors containing novel bacterial consortium (KDDBO4, KDDBO5, KDDBO8 and KDDB11) and its effect on Phytotoxicity. Res J Chem Environ 23:3

Kashefi S, Borghei SM, Mahmoodi NM (2019) Covalently immobilized laccase onto graphene oxide nanosheets: preparation, characterization, and biodegradation of azo dyes in colored wastewater. J Mol Liq 276:153–162

Khan S, Abdul M (2015) Degradation of reactive black 5 dye by a newly isolated bacterium *Pseudomonas entomophila* BS1. Can J Microbiol 62(3):220–232

Kolekar YM, Konde PD, Markad VL et al (2013) Effective bioremoval and detoxification of textile dye mixture by *Alishewanella* sp. KMK6. Appl Microbiol Biotechnol 97(2):881–889

Krishnamoorthy R, Jose PA, Ranjith M, Anandha R, Suganya K, Prabhakaran J, Kumutha K (2018) Decolourisation and degradation of azo dyes by mixed fungal culture consisted of *Dichotomomyces cejpii* MRCH 1-2 and *Phoma tropica* MRCH 1-3. J Environ Chem Eng 6(1):588–595

Kurade MB, Waghmode TR, Xiong JQ, Govindwar SP, Jeon BH (2019) Decolorization of textile industry effluent using immobilized consortium cells in upflow fixed bed reactor. J Clean Prod 213:884–891. https://doi.org/10.1016/j.jclepro.2018.12.218

Lade H, Kadam A, Paul D, Govindwar S (2015) Biodegradation and detoxification of textile azo dyes by bacterial consortium under sequential microaerophilic/aerobic processes. EXCLI J 14:158

Li WY, Chen FF, Wang SL (2010) Binding of reactive brilliant red to human serum albumin: insights into the molecular toxicity of sulfonic azo dyes. Protein Pept Lett 17(5):621–629

Lucas MS, Peres JA (2006) Decolorization of the azo dye reactive black 5 by Fenton and photo-Fenton oxidation. Dyes Pigments 71(3):236–244

Madkour LH, Kaya S, Kaya C, Guo L (2016) Quantum chemical calculations, molecular dynamics simulation and experimental studies of using some azo dyes as corrosion inhibitors for iron. Part 1: Mono-azo dye derivatives. J Taiwan Inst Chem Eng 68:461–480

Mahmood S, Khalid A, Arshad M, Mahmood T, Crowley DE (2016) Detoxification of azo dyes by bacterial oxidoreductase enzymes. Crit Rev Biotechnol 36(4):639–651

Mani A, Hameed SAS (2019) Improved bacterial-fungal consortium as an alternative approach for enhanced decolourisation and degradation of Azo dyes: a review. Nat Environ Pollut Technol 18(1):49–64

Mansour HB, Ayed-Ajmi Y, Mosrati R, Corroler D, Ghedira K, Barillier D, Chekir-Ghedira L (2010) Acid violet 7 and its biodegradation products induce chromosome aberrations, lipid peroxidation, and cholinesterase inhibition in mouse bone marrow. Environ Sci Pollut Res 17(7):1371–1378

Masarbo RS, Niranjana SR, Monisha TR, Nayak AS, Karegoudar TB (2019) Efficient decolorization and detoxification of sulphonated azo dye Ponceau 4R by using single and mixed bacterial consortia. Biocatal Biotransformation 37:1–10

Mehta R, Singhal P, Singh H, Damle D, Sharma AK (2016) Insight into thermophiles and their wide-spectrum applications. 3Biotech 6(1):1–9

Miran W, Nawaz M, Kadam A, Shin S, Heo J, Jang J, Lee DS (2015) Microbial community structure in a dual chamber microbial fuel cell fed with brewery waste for azo dye degradation and electricity generation. Environ Sci Pollut Res 22(17):13477–13485

Mohammad-Salehi H, Hamadanian M, Safardoust-Hojaghan H (2019) Visible-light induced Photodegradation of methyl Orange via palladium nanoparticles anchored to chrome and nitrogen doped TiO_2 nanoparticles. J Inorg Organomet Polym Mater 1–9

Munir E, Priyani N, Suryanto D, Naimah Z (2017) Using biomass of basidiomycetous fungi in decolorization of wastewater of textile industry. J Pure Appl Microbiol 11(2):669–676

Ortiz-Monsalve S, Dornelles J, Poll E, Ramirez-Castrillon M, Valente P, Gutterres M (2017) Biodecolourisation and biodegradation of leather dyes by a native isolate of *Trametes villosa*. Process Saf Environ Prot 109:437–451

Ortiz-Monsalve S, Valente P, Poll E, Jaramillo-García V, Henriques JAP, Gutterres M (2019) Biodecolourization and biodetoxification of dye-containing wastewaters from leather dyeing by the native fungal strain *Trametes villosa* SCS-10. Biochem Eng J 141:19–28

Puvaneswari N, Muthukrishnan J, Gunasekaran P (2006) Toxicity assessment and microbial degradation of azo dyes. Indian J Exp Biol 44(8):618–626

Rekik H, Jaouadi NZ, Bouacem K, Zenati B, Kourdali S, Badis A, Jaouadi B (2019) Physical and enzymatic properties of a new manganese peroxidase from the white-rot fungus *Trametes pubescens* strain i8 for lignin biodegradation and textile-dyes biodecolorization. Int J Biol Macromol 125:514–525

Rodríguez-Couto S (2019) Fungal Laccase: a versatile enzyme for biotechnological applications. In: Recent advancement in white biotechnology through Fungi. Springer, Cham, pp 429–457

Russ R, Rau J, Stolz A (2000) The function of cytoplasmic flavin reductases in the reduction of azo dyes by bacteria. Appl Environ Microbiol 66(4):1429–1434

Santos A, Mendes S, Brissos V, Martins LO (2014) New dye-decolorizing peroxidases from *Bacillus subtilis* and *Pseudomonas putida* MET94: towards biotechnological applications. Appl Microbiol Biotechnol 98:2053–2065. https://doi.org/10.1007/s00253-013-5041-4

Sarkar S, Banerjee A, Halder U, Biswas R, Bandopadhyay R (2017) Degradation of synthetic azo dyes of textile industry: a sustainable approach using microbial enzymes. Water Conserv Sci Eng 2(4):121–131

Sayahi E, Ladhari N, Mechichi T, Sakli F (2016) Azo dyes decolourization by the laccase from Trametes trogii. J Text Ins 107(11):1478–1482

Sen SK, Raut S, Bandyopadhyay P, Raut S (2016) Fungal decolouration and degradation of azo dyes: a review. Fungal Biol Rev 30(3):112–133

Sha Y, Mathew I, Cui Q, Clay M, Gao F, Zhang XJ, Gu Z (2016) Rapid degradation of azo dye methyl orange using hollow cobalt nanoparticles. Chemosphere 144:1530–1535

Siddique R, Alif FA (2018) Isolation and identification of orange M2R and green GS dye decolourizing Bacteria from textile sludge (soil) samples and determination of their optimum decolourization conditions. Ann Res Rev Biol 22:1–12

Singh P, Kumar R (2019) Critical review of microbial degradation of aromatic compounds and exploring potential aspects of Furfuryl alcohol degradation. J Polym Environ 27:1–16

Singh RL, Singh PK, Singh RP (2015) Enzymatic decolorization and degradation of azo dyes–a review. Int Biodeterior Biodegradation 104:21–31

Solís M, Solís A, Pérez HI, Manjarrez N, Flores M (2012) Microbial decolouration of azo dyes: a review. Process Biochem 47(12):1723–1748

Srivastava S, Sinha R, Roy D (2004) Toxicological effects of malachite green. Aquat Toxicol 66(3):319–329

Stolz A (2001) Basic and applied aspects in the microbial degradation of azo dyes. Appl Microbiol Biotechnol 56(1–2):69–80

Sudha M, Saranya A, Selvakumar G, Sivakumar N (2014) Microbial degradation of azo dyes: a review. Int J Curr Microbiol App Sci 3(2):670–690

Tochhawng L, Mishra VK, Passari AK, Singh BP (2019) Endophytic Fungi: role in dye Decolorization. In: Advances in Endophytic fungal research. Springer, Cham, pp 1–15

Vantamuri AB, Kaliwal BB (2016) Purification and characterization of laccase from Marasmius species BBKAV79 and effective decolorization of selected textile dyes. Biotech 6(3):189

Verma K, Saha G, Kundu LM, Dubey VK (2019) Biochemical characterization of a stable azoreductase enzyme from *Chromobacterium violaceum*: application in industrial effluent dye degradation. Int J Biol Macromol 121:1011–1018

Wang Q, Huang L, Quan X, Puma GL (2019) Sequential anaerobic and electro-Fenton processes mediated by W and Mo oxides for degradation/mineralization of azo dye methyl orange in photo assisted microbial fuel cells. Appl Catal B Environ 245:672–680

Wong Y, Yu J (1999) Laccase-catalyzed decolorization of synthetic dyes. Water Res 33(16):3512–3520

Wuhrmann K, Mechsner KL, Kappeler TH (1980) Investigation on rate—determining factors in the microbial reduction of azo dyes. Appl Microbiol Biotechnol 9(4):325–338

Zhang Y, Dong W, Lv Z, Liu J, Zhang W, Zhou J, Jiang M (2018) Surface display of bacterial Laccase CotA on *Escherichia coli* cells and its application in industrial dye Decolorization. Mol Biotechnol 60(9):681–689

Role of Interspecies Electron Transfer for Boosting Methane Production by Anaerobic Digestion in Syntrophic Methanogenesis

5

Hui Xu, Yanbiao Liu, Bo Yang, Ruihong Wei, Fang Li,
and Sand Wolfgang

Abstract

Addition of conductive materials to anaerobic sludge systems is an attractive strategy to enhance anaerobic metabolism and methane production. The presence of direct interspecies electron transfer (DIET) in microbial communities is commonly used to improve methane production, while the underlying mechanisms remain under debate. Though DIET has distinct advantages, the interspecies H_2/formate transfer in syntrophic metabolism is believed to be the main electron transfer pathway. This chapter presents an overview on fundamental mechanisms on interspecies electron transfer and the boosting effect of some conductive materials in bioengineered system with a particular focus on the improvement in methane production.

Keywords

Anaerobic digestion · Methane production · Conductive materials · DIET · Interspecies electron transfer

---

H. Xu · R. Wei
Textile Pollution Controlling Engineering Center of Ministry of Environmental Protection,
College of Environmental Science and Engineering, Donghua University,
Shanghai, P. R. China

Y. Liu (✉) · B. Yang · F. Li · S. Wolfgang
Textile Pollution Controlling Engineering Center of Ministry of Environmental Protection,
College of Environmental Science and Engineering, Donghua University,
Shanghai, P. R. China

Shanghai Institute of Pollution Control and Ecological Security, Shanghai, P. R. China
e-mail: yanbiaoliu@dhu.edu.cn

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_5

5.1 Introduction

Anaerobic digestion (AD) is a promising technology for application in wastewater treatment combined with energy recovery (Zhang et al. 2018a; Martins et al. 2018; Liu et al. 2019; Li et al. 2019a). To date, the wide application of AD technology is mostly limited by its poor energy conversion efficiency due to (i) limited amounts of methane in the biogas; (ii) unstable biogas production, which is susceptible to external conditions; and (iii) strict quality requirements for the influent wastewater (Hao et al. 2017). Furthermore, due to thermodynamic limitations of the AD process, syntrophic metabolic relations between digesting bacteria and methanogens are the basis for achieving a high methane production (Li et al. 2019b). The whole process can be summarized as follows: proteins, polysaccharide, volatile fatty acids (VFAs), and alcohols were degraded into short chain fatty acids (e.g., acetic acid, H_2, and formic acid) by fermenting bacteria. These compounds can then be utilized by methanogens for reducing CO_2 to methane (Li et al. 2019b). However, too much H_2 will limit the metabolic activity of the fermenters, since fermentation process is limited by high H_2 partial pressure (Zhang et al. 2018a). Thus, the interspecies H_2 transfer process from fermenters to methanogens is essential for the overall thermodynamics during AD. H_2-consuming methanogens produce methane and, in this way, maintain a low H_2 partial pressure. This promotes the anaerobic metabolism of VFAs. Thus, H_2 and formate act as electron shuttle during AD. However, the interspecies H_2/formate transfer between fermenters and methanogens can be easily blocked by diffusion limitations (Wang et al. 2019; Scoma et al. 2016).

An addition of selected metal oxides or their nanoparticles (NPs) has been proven to be effective to promote anaerobic metabolism by stimulating enzyme secretion and microbial growth (Zhang et al. 2018b; Tian et al. 2019; Cruz Viggi et al. 2014). Recent studies show that interspecies electron transfer is existing between bacteria and methanogens. It can be triggered by addition of certain conductive materials (Martins et al. 2018; Zhao et al. 2017; Lee et al. 2016). Reports indicate that after an addition of granular activated carbon (GAC), the electron transfer rate is 10^6 times higher than the one for an interspecies H_2/formate transfer without addition (Zhang et al. 2018a; Martins et al. 2018). Moreover, an addition of GAC also avoids the energy to produce extracellular conductive pili and/or c-type cytochromes, which are providing electrical connections between cells (Martins et al. 2018). Therefore, the interspecies electron transfer may function in a way that the methane yield becomes improved (Martins et al. 2018; Zhao et al. 2015). However, solid evidence for DIET was only observed for cocultures of exoelectrogenic bacteria, but not all syntrophic bacteria have been shown to have the capability of DIET.

In this chapter, we aim to review the recent advances in boosting AD performance by conductive materials by focusing on the interspecies electron transfer. Firstly, the fundamental mechanisms of interspecies electron transfer in a typical AD process are described. Then, the underlying mechanisms of the boosting effect of carbon-based materials, metal oxides, and composites are discussed. Finally, future perspectives and challenges of DIET are provided as well.

5.2 Interspecies Electron Transfer in Syntrophic Methanogenic Associations of Microorganisms

5.2.1 Interspecies Electron Transfer via H_2/Formate

Interspecies H_2/formate transfer is regarded as the most well-known mechanism of electron transfer in methanogenic communities (Fig. 5.1a)[12]. H_2 can be used as a direct electron donor for CO_2 conversion to produce methane by H_2-consuming methanogens. The interspecies H_2 transfer between syntrophic bacteria and methanogens is ubiquitous in the AD process (Martins et al. 2018). This is attributed to the small molecular weight and ease of diffusion for H_2 (Li et al. 2019b). Syntrophic fermenting microorganic can use protons as electron acceptors to produce H_2 from NADH, $FADH_2$, and other redox intermediates (Jin et al. 2019; Li et al. 2018; Stams and Plugge 2009). However, these reactions only occur at low H_2 partial pressure due to the limited redox potential of H^+/H_2 ($E°' = -414$ mV). Thus, H_2 scavengers are needed to avoid H_2 accumulation. Energetics of H_2/formate-related reactions in syntrophic cultures with methanogens are summarized in Table 5.1. It is noteworthy that the consumption of H_2 by methanogens will decrease the H_2 partial pressure.

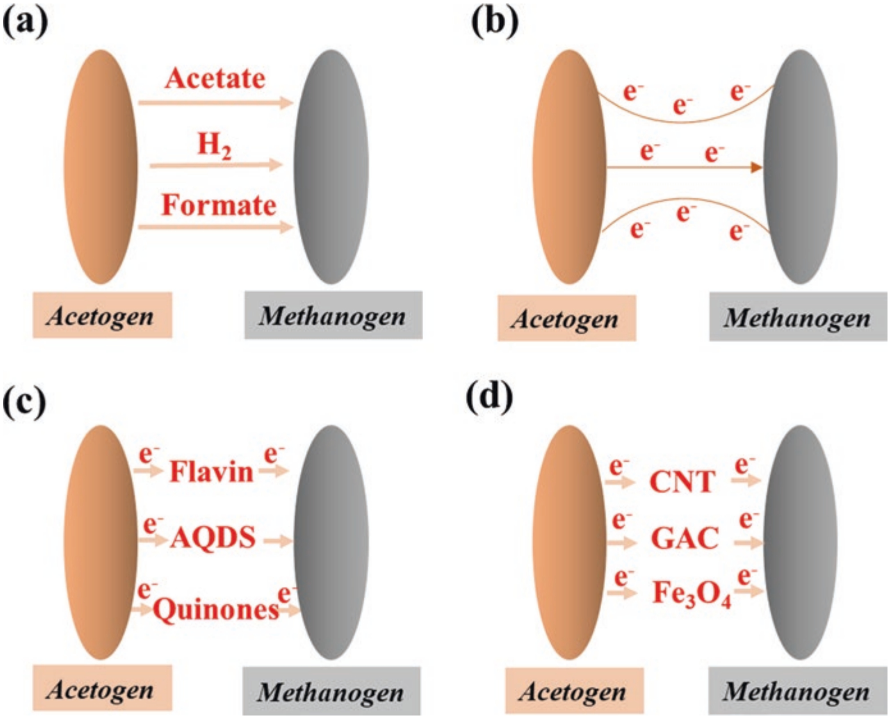


Fig. 5.1 Possible interspecies electron transfer mechanisms between syntrophic microorganisms and methanogens. (Image is modified from Martins et al. (2018))

Table 5.1 Energetics of H_2/formate-related reactions in syntrophic methanogenesis (Stams and Plugge 2009)

Reaction	$\Delta G^{\circ\prime}$ (kJ/moL)	$\Delta G'$ (kJ/moL)
Syntrophic microorganisms		
Formate+$H^+ \rightarrow CO_2+H_2$	−3	−32
NADH+$H^+ \rightarrow NAD^+ + H_2$	+18	−11
$FADH_2 \rightarrow FAD+H_2$	+37	+8
Methanogens		
$H_2+F_{420} \rightarrow F_{420}\text{-}H_2$	−11	+18
$4HCOO^- + 4H^+ \rightarrow$ Methane$+3CO_2+2H_2O$	−119.5	–

Note: $\Delta G^{\circ\prime}$ is calculated for standard state and $\Delta G'$ at a 1 kPa

This promotes syntrophic fermenting microorganisms to produce H_2. Thus, interspecies H_2 transfer between syntrophic fermenting microorganisms and methanogens is critical for converting organic compound into methane.

Besides H_2, formate is another important interspecies electron transfer compound in the syntrophic methanogenic process (Fig. 5.1a). Several reports indicate that an obvious gap between the H_2 diffusion rate and the methane production rate was observed under natural conditions. This indicates that interspecies formate transfer is indeed existing. Another reason is that there is little difference between the redox potential of formate/CO_2 (−414 mV) versus that of H^+/H_2 (−432 mV). Therefore, it is reasonable to conclude that interspecies electron transfers via H_2 and formate are essential for syntrophic methanogenic microbial associations (Zhang et al. 2018a; Hao et al. 2017). However, it is still unknown which process dominates in the interspecies electron transfer. Several studies confirmed the interspecies H_2 or formate transfer co-exist. The contribution of the two interspecies electron transfer pathways in the syntrophic methanogenic process requires further study.

5.2.2 Direct Interspecies Electron Transfer (DIET)

Besides interspecies H_2 or formate transfer, another type of DIET occurs between syntrophic microorganisms and methanogens during AD. Electron-capturing microorganisms can accept directly electrons from exoelectrogenic microorganisms by a DIET process (Zhao et al. 2016, 2017). There are currently few proposed theories regarding the mechanism of extracellular electron transfer: (i) electrons are transferred directly to acceptors via a solute cytochrome c to the outer membrane. Recent studies have shown that the content of solute cytochrome c in *G. sulfurreducens* grown on low-iron medium was decreased, resulting to an inhibition of the extracellular electron transport (Estevez-Canales et al. 2015). This proves the necessity of a solute cytochrome c for an extracellular electron transport; (ii) another proposed theory is DIET by electrically conductive pili or by direct contact (Fig. 5.1b). Reguera et al. proved that the pili of *G. sulfurreducens* possess excellent conductivity and can act as a biological nanowire for electron transfer from the cell to extracellular Fe(III) oxides (Reguera et al. 2005). This also predicts that electrons can be transferred between cells through pili (Rotaru et al. 2014a). They also claimed electrons released by *Geobacter* can be transferred *via* pili directly to *Methanosaeta* (Rotaru et al. 2014a). However, how these electrons are taken up by the methanogens is not yet known; (iii) next is extracellular electron transfer via extracellular shuttle molecules. Oxidized shuttle molecules receive electrons, which reduces the shuttle molecules. The electrons are transferred to the outer membrane, where an exited acceptor molecule is accepting them (becoming reduced) (Tian et al. 2017). Unlike H_2 or formate which penetrates the cell, these extracellular electron shuttle molecules remain extracellular, meaning that they do not diffuse in and out the cell (e.g., humic acids (HS), anthraquinone-2,6-disulfonate (AQDS) (Rabaey et al. 2005), phenazine (Okamoto et al. 2013), flavin, and quinones (Newman and Kolter 2000)) (Fig. 5.1c). For the syntrophic methanogenic process, recent studies have shown that DIET is mainly dependent on pili and solute cytochrome c. Rotaru et al. designed a coculture system for pure culture experiments with *G. metallireducens*, *Pelobacter carbinolicus*, and *Methanosarcina barkeri* to evaluate the ability of *M. barkeri* to use DIET (Rotaru et al. 2014b). Results indicate that DIET and interspecies H_2 or formate transfer occur simultaneously for this methanogen. In addition, a syntrophic metabolism between *G. metallireducens* and *M. barkeri* is not possible due to the lack of pili in *G. metallireducens*. However, a syntrophic metabolism using the DIET can be restored by an addition of GAC. This finding suggests that externally added conductive adducts can replace the natural ones (like pili) in DIET (Fig. 5.1d). In fact, several studies have confirmed that conductive materials can promote DIET in syntrophic methanogenic cocultures like magnetite particles (Zhao et al. 2018), biochar (BC) (Fagbohungbe et al. 2016), or carbon cloth (CC) (Lei et al. 2016).

In addition to carbon-based materials, iron-based materials (e.g., iron-manganese bi-metal oxides, iron oxides, and zero-valent iron (ZVI)) have been used as additives in both batch and continuous anaerobic bioreactors to improve DIET. Yin et al. illustrated that the addition of Fe_3O_4 to an anaerobic reactor enhanced both the maximum methane production rate and yield (Yin et al. 2018). These results can be attributed to an increase of the conductivity between microorganisms in the anaerobic sludge, because of the improved extracellular electron transfer due to Fe_3O_4 addition. MnO_2 NPs are also capable to stimulate the methane yield. The methanogens utilize the electrons released from Mn^{2+} oxidation to produce methane from CO_2 (Tian et al. 2017). In addition, ZVI also has been reported to enhance methane production in AD. Three pathways were proposed for the enhancement effect by iron: (Hao et al. 2017) (i) the addition of iron reduces the ORP which would change propionate-type fermentation to acetate-type fermentation; (ii) additional H_2 production derived from iron dissolution is favorable for both hydrogenotrophic methanogenesis and homoacetogenesis; and (iii) anaerobic enzyme activity can be stimulated by addition of iron ions. Recently, Zhao et al. compared the difference of ZVI or Fe_3O_4 addition for activated sludge anaerobic digestion (Zhao et al. 2018). The results indicate that the addition of Fe_3O_4 had a positive impact on acidogenic phase, if compared with ZVI. However, Fe_3O_4 inhibited hydrogenotrophic methanogenesis and, hence, decreased methane production. In contrast, ZVI obviously promoted the hydrogenotrophic methanogenic phase. Zhang et al. observed that composite conductive materials GAC/ZVI can enhance the conversion of antibiotics and methane production in AD (Zhang et al. 2018c). Previous studies mostly used a single mediator to promote AD and methane production (Zhang et al. 2018a; He et al. 2017). Moreover, a direct inoculation of metal oxide NPs into an anaerobic system may lead to an agglomeration and flocculation of the sludge. Drawbacks such as wash-out and poor mass transfer are inevitable (Tian et al. 2017; Zhang et al. 2018c). Thus, whether composite mediators have a positive effect on the AD deserves further investigations.

5.3 Effect of Conductive Materials on Methane Production

5.3.1 Carbon-Based Conductive Materials

Several strategies have been pursued to improve AD. Recently, the use of conductive materials is considered to be a good possibility to enhance methane production and the stability of the anaerobic system. The most common conductive materials applied to AD systems are GAC and magnetite, followed by carbon nanotubes (CNT) (Li et al. 2015; Wasim et al. 2019), biochar (BC) (Fagbohungbe et al. 2016), or carbon cloth (CC) (Lei et al. 2016).

VFAs play key roles in AD by regulating the pH of the anaerobic system and affecting microbial activity (Xu et al. 2018). The activity of methanogens can be inhibited severely by VFA accumulation. Some carbon-based materials have a buffering capacity during the AD. For instance, the addition of BC can maintain the medium in the proper pH range for both acidification stage and the methanogenic stage and increase the methane yield (Jing et al. 2017; Luo et al. 2015). The addition of these carbon materials also helps to maintain a stable syntrophic metabolism and an acid balance, if under acidic shock. This guarantees a stable metabolic activity of the syntrophic methanogenic association. Moreover, several studies reported that the addition of carbon-based materials promotes VFA production in an anaerobic fermentation reactor, while the accumulation of VFAs was decreased with the addition of carbon-based materials, if complex wastewaters were treated by the AD process (Wang et al. 2019; Lei et al. 2016; Liu et al. 2012).

The operational parameters for different types of carbon-based materials and their effect on methane production in AD are summarized in Table 5.2. Lee et al. indicated that the methane yield increased by 78% due to the addition of GAC (Lee et al. 2016). Similarly, Zhao et al. reported that the methane production in a CNT-supplemented reactor doubled compared with the control (Li et al. 2015). It seems that the boosting performance is a specific result of the morphology of the added material. Although those materials are mainly composed of carbon, their different physicochemical characteristics (e.g., BET surface area or electrical conductivity) cause different boosting effects. Since these material characteristics directly affect

Table 5.2 Effect of carbon-based materials on methane production in AD

Inoculum	Substrates	Material	Applied conc. (g/L)	Methane yield rate improvement (%)	References
Anaerobic sludge	Acetate	GAC	1.0	80.0	Lee et al. (2016)
Activated sludge	Ethanol	GAC	20	14	Feng et al. (2014)
Anaerobic sludge	Glucose	GAC	40	59	Abdelsalam et al. (2016)
Anaerobic sludge	Glucose	CNT	1.0	100	Li et al. (2015)
Anaerobic sludge	Citrus peel	BC	35	12	Fagbohungbe et al. (2016)
Anaerobic sludge	Ethanol	BC	1.25	30-45	Zhao et al. (2015)
Anaerobic sludge	Glucose	BC	10	21	Luo et al. (2015)
Anaerobic sludge	Leachate	CC	(833 cm^2/L)	30	Lei et al. (2016)
Anaerobic sludge	Butanol	CC	(500 cm^2/L)	59	Zhao et al. (2017)

the activity and distribution of the microorganisms, different metabolic pathways and methane production are resulting. On the other hand, the concentration and type of substrate also affect methane yield. Generally, there was an obvious increase of the methane yield, if carbon-based materials were added to the anaerobic sludge system. This means that increased organic loading rates can be treated by anaerobic digesters with the aid of carbon-based materials. Despite several studies, which confirmed that carbon-based materials have a positive impact on methane production, the mechanisms for an enhancement of the methanogenic activity are still unknown. It has been reported that the enhancement might be attributed to a change of the ORP during methanogenesis with carbon-based materials (Hao et al. 2017; Feng et al. 2014). On the other hand, the electrical conductivity of the anaerobic biomass or granules would change in the presence of carbon-based materials (Zhang et al. 2018a). Also, the metabolism and composition of the anaerobic microbial communities will change due to the differences in electrical conductivity in the presence of carbon-based materials.

5.3.2 Metal Oxides

In addition to carbon-based materials, several metal oxides and their nanoparticles have also been found to accelerate anaerobic hydrolysis and methane production (Abdelsalam et al. 2016). Moreover, metal oxide materials are inexpensive and easily available from industry. As shown in Fig. 5.2, materials like magnetite NPs enhanced methane production through facilitating DIET (Jing et al. 2017; Peng

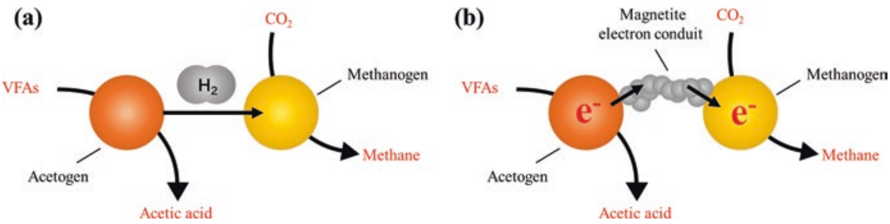


Fig. 5.2 Simplified schedules for electron transfer pathways in methane formation of interspecies H_2 transfer (**a**) and DIET with magnetite addition (**b**). (Image is created based on Cruz Viggi et al. (2014)

et al. 2018). Recent studies indicate that conductive Fe (II/III) oxides exhibit an ideal potential for improving the degradation of complex organic compounds and for increasing methane production (Zhao et al. 2018; Cruz Viggi et al. 2014). In addition, iron nanoparticles have been shown to improve methanogenic activity and to produce a more stabilized sludge. ZVI has a low oxidation-reduction potential ($E_0 = -0.44$ V), which provides a favorable environment for methanogens (Hassanein et al. 2019). Moreover, dissolution productions like $Fe(OH)_2$ or $Fe(OH)_3$ act as buffer maintaining a suitable pH in anaerobic systems. Furthermore, ZVI is an effective electron donor. H_2 is produced during iron dissolution. This H_2 can be used by methanogens and increases methane production (Hao et al. 2017; Feng et al. 2014). In addition, ZVI can increase the microbial activity (Feng et al. 2014). Table 5.3 summarizes several studies with metal oxide materials and the corresponding performance in AD. Zhao et al. showed that the methane yield increased by 44% with the addition of Fe_3O_4 NPs (Zhao et al. 2018). Feng et al. observed that the addition of ZVI also promotes methane production (Feng et al. 2014). Because of availability and price, iron and iron oxides are the most used metallic materials for improving methane production. Recent studies suggest that methanogens can utilize electrons released by the oxidation of Mn^{2+} ions and subsequently convert CO_2 into methane (Tian et al. 2017). On the other hand, several studies indicate also that the activity of methanogens can be inhibited, if adding an excess of metal oxides into an anaerobic sludge system.

5.3.3 Composite Materials

There are only few studies available on the effect of composite materials on methanogens during AD. Recent studies show that composite materials possess unique advantages over single materials (Zhang et al. 2015, 2018c, 2019; Qin et al. 2017). Table 5.4 summarizes available studies using composite materials to boost AD performance. So far, research on composite materials has been relatively rare due to the complexity of the system. The most common composite materials are mixtures of

Table 5.3 Overview on the use of the metal oxide or its nanoparticles in AD

Material	Inoculum	Substrates	Applied conc. (mg/L)	Methane improvement (%)	References
Fe_3O_4	Anaerobic sludge	Activated sludge	27000	7.3[a]	Peng et al. (2018)
Fe_3O_4	Anaerobic sludge	Activated sludge	10000	29.9[a]	Zhao et al. (2018)
Fe_3O_4 NPs	Anaerobic sludge	Propionate	10	44[a]	Jing et al. (2017)
Fe^0	Anaerobic sludge	Activated sludge	10000	21.3[a]	Zhang et al. (2015)
Fe^0	Anaerobic sludge	Activated sludge	20000	43.5[a]	Feng et al. (2014)
Fe^0 NPs	Anaerobic sludge	Poultry litter	100	29.1[a]	Hassanein et al. (2019)
Fe^0 NPs	Anaerobic sludge	Fresh manure	20	67[b]	Abdelsalam et al. (2016)
MnO_2 NPs	Anaerobic sludge	Activated sludge	400	42[b]	Tian et al. (2017)
MnO_2 NPs	Anaerobic sludge	Activated sludge	60	25.6[b]	Tian et al. (2019)

Note: [a] CH_4 production, [b] CH_4 production rate

Table 5.4 Summary of potential effect of composite materials on the performance of AD

	Materials		Operational conditions			
Inoculum	Material I	Material II	Substrates	Temp (°C)	Increase in methane yield/rate (%)	References
Anaerobic sludge	Fe_3O_4	GAC	Activated sludge	37	20	Peng et al. (2018)
Anaerobic sludge	Fe_3O_4	BC	Activated sludge	35	12	Qin et al. (2017)
Granular sludge	ZVI	GAC	Tetracycline	35	73	Zhang et al. (2018c)
Anaerobic sludge	nZVI	BC	Sewage sludge	37	15	Zhang et al. (2019)

iron oxides with carbon-based materials. However, most composite materials are composed of different kinds of materials. The impact of such synthetic materials on AD and methane production remains to be elucidated in the future. Zhang et al. discuss that the addition of the composite GAC/ZVI as mediator of electron transport not only enhances the AD and methane production but also decreases the loss of Fe compounds (Zhang et al. 2018c).

5.4 Current Challenges and Future Perspectives

Though many studies have demonstrated the presence of DIET, at present, only 12 pairs of syntrophic microorganisms have been proven to participate in DIET. Obviously, not all syntrophic bacteria are capable of using DIET. Moreover, in each pair of syntrophic microorganisms, a *Geobacter* strain is present. Thus, it seems as if *Geobacter* would be essential as participant for DIET. However, Luo et al. found that the accumulation of VFAs was significantly reduced with the addition of BC, while the methane production was enhanced (Luo et al. 2015). However, in this experiment, *Geobacter* was not detected on the surface of BC by sequence analysis of the microbial community. This suggests that the boosting mechanism of BC in this sludge system is still unclear. In addition, the abundance of *Geobacter* was very low and even undetectable in some anaerobic reactors. This finding suggests that DIET does not always participate in AD. Thus, the scarcity of microbial species, which can participate in DIET, limits its general application. Furthermore, it has been reported that only a few substrates can be used as electron donors or acceptors for DIET (e.g., ethanol, propanol, butanol, acetate, formate, CO_2, and nitrate) (Luo et al. 2015). Therefore, the focus of current research is to investigate the effect of conductive materials for the syntrophic methanogenic microorganisms.

Interspecies electron transfer is of vital importance for syntrophic methanogenic processes. However, several key problems remain unresolved:

1. To find additional electron acceptors for interspecies electron transport. Discovering new substrates and electron acceptors of microorganism.
2. To purify high-efficiency exoelectrogenic bacteria. Only a small number of microorganisms have been reported to have the function of transferring electrons. Moreover, electron transfer efficiency is low, limiting the application for the treatment of wastewater.
3. To unveil the mechanisms of interspecies electron transfer at molecular level. Fundamental studies on the molecular properties of the essential components are missing. Data will provide an improved understanding of this complicated process.
4. To investigate interspecies electron transfer under real conditions. Which microorganisms will participate under different environmental conditions? Which member of the biocoenosis is the dominant one?
5. To develop more cheap conductive materials to promote electron transfer.

Acknowledgments This work was supported by Shanghai Science and Technology Committee (No. 19DZ1204900), the Shanghai Pujiang Program (No. 18PJ1400400), the Natural Science Foundation of Shanghai, China (No. 18ZR1401000), and the National Key Research and Development Program of China (No. 2018YFF0215703).

References

Abdelsalam E, Samer M, Attia YA, Abdel-Hadi MA, Hassan HE, Badr Y (2016) Comparison of nanoparticles effects on biogas and methane production from anaerobic digestion of cattle dung slurry. Renew Energy 87:592–598

Cruz Viggi C, Rossetti S, Fazi S, Paiano P, Majone M, Aulenta F (2014) Magnetite particles triggering a faster and more robust syntrophic pathway of methanogenic propionate degradation. Environ Sci Technol 48(13):7536–7543

Estevez-Canales M, Kuzume A, Borjas Z, Fueg M, Lovley D, Wandlowski T, Esteve-Nunez A (2015) A severe reduction in the cytochrome C content of Geobacter sulfurreducens eliminates its capacity for extracellular electron transfer. Environ Microbiol Rep 7(2):219–226

Fagbohungbe MO, Herbert BMJ, Hurst L, Li H, Usmani SQ, Semple KT (2016) Impact of biochar on the anaerobic digestion of citrus peel waste. Bioresour Technol 216:142–149

Feng Y, Zhang Y, Quan X, Chen S (2014) Enhanced anaerobic digestion of waste activated sludge digestion by the addition of zero valent iron. Water Res 52:242–250

Hao X, Wei J, van Loosdrecht MCM, Cao D (2017) Analysing the mechanisms of sludge digestion enhanced by iron. Water Res 117:58–67

Hassanein A, Lansing S, Tikekar R (2019) Impact of metal nanoparticles on biogas production from poultry litter. Bioresour Technol 275:200–206

He CS, He PP, Yang HY, Li LL, Lin Y, Mu Y, Yu HQ (2017) Impact of zero-valent iron nanoparticles on the activity of anaerobic granular sludge: from macroscopic to microcosmic investigation. Water Res 127:32–40

Jin Z, Zhao Z, Zhang Y (2019) Potential of direct interspecies electron transfer in synergetic enhancement of methanogenesis and sulfate removal in an up-flow anaerobic sludge blanket reactor with magnetite. Sci Total Environ 677:299–306

Jing Y, Wan J, Angelidaki I, Zhang S, Luo G (2017) iTRAQ quantitative proteomic analysis reveals the pathways for methanation of propionate facilitated by magnetite. Water Res 108:212–221

Lee J-Y, Lee S-H, Park H-D (2016) Enrichment of specific electro-active microorganisms and enhancement of methane production by adding granular activated carbon in anaerobic reactors. Bioresour Technol 205:205–212

Lei Y, Sun D, Dang Y, Chen H, Zhao Z, Zhang Y, Holmes DE (2016) Stimulation of methanogenesis in anaerobic digesters treating leachate from a municipal solid waste incineration plant with carbon cloth. Bioresour Technol 222:270–276

Li L-L, Tong Z-H, Fang C-Y, Chu J, Yu H-Q (2015) Response of anaerobic granular sludge to single-wall carbon nanotube exposure. Water Res 70:1–8

Li Y, Xu D, Chen C, Li X, Jia R, Zhang D, Sand W, Wang F, Gu T (2018) Anaerobic microbiologically influenced corrosion mechanisms interpreted using bioenergetics and bioelectrochemistry: a review. J Mater Sci Technol 34(10):1713–1718

Li M, Liu Y, Dong L, Shen C, Li F, Huang M, Ma C, Yang B, An X, Sand W (2019a) Recent advances on photocatalytic fuel cell for environmental applications—the marriage of photocatalysis and fuel cells. Sci Total Environ 668:966–978

Li Y, Chen Y, Wu J (2019b) Enhancement of methane production in anaerobic digestion process: a review. Appl Energy 240:120–137

Liu Y, Zhang Y, Quan X, Li Y, Zhao Z, Meng X, Chen S (2012) Optimization of anaerobic acidogenesis by adding Fe^0 powder to enhance anaerobic wastewater treatment. Chem Eng J 192:179–185

Liu Y, Wu P, Liu F, Li F, An X, Liu J, Wang Z, Shen C, Sand W (2019) Electroactive modified carbon nanotube filter for simultaneous detoxification and sequestration of Sb(III). Environ Sci Technol 53(3):1527–1535

Luo C, Lu F, Shao L, He P (2015) Application of eco-compatible biochar in anaerobic digestion to relieve acid stress and promote the selective colonization of functional microbes. Water Res 68:710–718

Martins G, Salvador AF, Pereira L, Alves MM (2018) Methane production and conductive materials: a critical review. Environ Sci Technol 52(18):10241–10253

Newman DK, Kolter R (2000) A role for excreted quinones in extracellular electron transfer. Nature 405(6782):94–97

Okamoto A, Hashimoto K, Nealson KH, Nakamura R (2013) Rate enhancement of bacterial extracellular electron transport involves bound flavin semiquinones. Proc Natl Acad Sci U S A 110(19):7856–7861

Peng H, Zhang Y, Tan D, Zhao Z, Zhao H, Quan X (2018) Roles of magnetite and granular activated carbon in improvement of anaerobic sludge digestion. Bioresour Technol 249:666–672

Qin Y, Wang H, Li X, Cheng JJ, Wu W (2017) Improving methane yield from organic fraction of municipal solid waste (OFMSW) with magnetic rice-straw biochar. Bioresour Technol 245:1058–1066

Rabaey K, Boon N, Hofte M, Verstraete W (2005) Microbial phenazine production enhances electron transfer in biofuel cells. Environ Sci Technol 39(9):3401–3408

Reguera G, McCarthy KD, Mehta T, Nicoll JS, Tuominen MT, Lovley DR (2005) Extracellular electron transfer via microbial nanowires. Nature 435(7045):1098–1101

Rotaru A-E, Shrestha PM, Liu F, Shrestha M, Shrestha D, Embree M, Zengler K, Wardman C, Nevin KP, Lovley DR (2014a) A new model for electron flow during anaerobic digestion: direct interspecies electron transfer to Methanosaeta for the reduction of carbon dioxide to methane. Energy Environ Sci 7(1):408–415

Rotaru AE, Shrestha PM, Liu F, Markovaite B, Chen S, Nevin KP, Lovley DR (2014b) Direct interspecies electron transfer between Geobacter metallireducens and Methanosarcina barkeri. Appl Environ Microbiol 80(15):4599–4605

Scoma A, Varela-Corredor F, Bertin L, Gostoli C, Bandini S (2016) Recovery of VFAs from anaerobic digestion of dephenolized olive mill wastewaters by electrodialysis. Sep Purif Technol 159:81–91

Stams AJM, Plugge CM (2009) Electron transfer in syntrophic communities of anaerobic bacteria and archaea. Nat Rev Microbiol 7:568

Tian T, Qiao S, Yu C, Tian Y, Yang Y, Zhou J (2017) Distinct and diverse anaerobic respiration of methanogenic community in response to MnO_2 nanoparticles in anaerobic digester sludge. Water Res 123:206–215

Tian T, Qiao S, Yu C, Zhou J (2019) Effects of nano-sized MnO_2 on methanogenic propionate and butyrate degradation in anaerobic digestion. J Hazard Mater 364:11–18

Wang G, Li Q, Gao X, Wang XC (2019) Sawdust-derived biochar much mitigates VFAs accumulation and improves microbial activities to enhance methane production in thermophilic anaerobic digestion. ACS Sustain Chem Eng 7(2):2141–2150

Wasim M, Sabir A, Shafiq M, Khan RU (2019) Fractionation of direct dyes using modified vapor grown carbon nanofibers and zirconia in cellulose acetate blend membranes. Sci Total Environ 677:194–204

Xu H, Liu Y, Gao Y, Li F, Yang B, Wang M, Ma C, Tian Q, Song X, Sand W (2018) Granulation process in an expanded granular sludge blanket (EGSB) reactor for domestic sewage treatment: impact of extracellular polymeric substances compositions and evolution of microbial population. Bioresour Technol 269:153–161

Yin Q, Yang S, Wang Z, Xing L, Wu G (2018) Clarifying electron transfer and metagenomic analysis of microbial community in the methane production process with the addition of ferroferric oxide. Chem Eng J 333:216–225

Zhang L, Zhang L, Li D (2015) Enhanced dark fermentative hydrogen production by zero-valent iron activated carbon micro-electrolysis. Int J Hydrog Energy 40(36):12201–12208

Zhang J, Zhao W, Zhang H, Wang Z, Fan C, Zang L (2018a) Recent achievements in enhancing anaerobic digestion with carbon- based functional materials. Bioresour Technol 266:555–567

Zhang F, Hou J, Miao L, Chen J, Xu Y, You G, Liu S, Ma J (2018b) Chlorpyrifos and 3,5,6-trichloro-2-pyridinol degradation in zero valent iron coupled anaerobic system: performances and mechanisms. Chem Eng J 353:254–263

Zhang Z, Gao P, Cheng J, Liu G, Zhang X, Feng Y (2018c) Enhancing anaerobic digestion and methane production of tetracycline wastewater in EGSB reactor with GAC/NZVI mediator. Water Res 136:54–63

Zhang M, Li JH, Wang YC (2019) Impact of biochar-supported zerovalent iron nanocomposite on the anaerobic digestion of sewage sludge. Environ Sci Pollut Res 26(10):10292–10305

Zhao Z, Zhang Y, Woodard TL, Nevin KP, Lovley DR (2015) Enhancing syntrophic metabolism in up-flow anaerobic sludge blanket reactors with conductive carbon materials. Bioresour Technol 191:140–145

Zhao Z, Zhang Y, Yu Q, Dang Y, Li Y, Quan X (2016) Communities stimulated with ethanol to perform direct interspecies electron transfer for syntrophic metabolism of propionate and butyrate. Water Res 102:475–484

Zhao Z, Zhang Y, Li Y, Dang Y, Zhu T, Quan X (2017) Potentially shifting from interspecies hydrogen transfer to direct interspecies electron transfer for syntrophic metabolism to resist acidic impact with conductive carbon cloth. Chem Eng J 313:10–18

Zhao Z, Zhang Y, Li Y, Quan X, Zhao Z (2018) Comparing the mechanisms of ZVI and Fe_3O_4 for promoting waste-activated sludge digestion. Water Res 144:126–133

Recent Advances in Physicochemical and Biological Treatment Approaches for Distillery Wastewater

6

Vineet Kumar, Ram Chandra, Indu Shekhar Thakur,
Gaurav Saxena, and Maulin P. Shah

Abstract

Molasses-based distilleries are amongst the most polluting industries worldwide generating huge volume of high strength wastewater. Discharge of this wastewater, enriched with toxic androgenic and carcinogenic pollutants including melanoidins, phenolics, endocrine disrupting chemicals, organic acids, heavy metals and other recalcitrant hazardous compounds, into the environment without adequate treatment posing a risk to human, animals, microorganisms, and plants.

V. Kumar (✉)
Environmental Microbiology and Biotechnology Laboratory, School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, India

Department of Environmental Microbiology (DEM), Babasaheb Bhimrao Ambedkar (Central) University, Lucknow, Uttar Pradesh, India

R. Chandra
Department of Environmental Microbiology (DEM), Babasaheb Bhimrao Ambedkar (Central) University, Lucknow, Uttar Pradesh, India

I. S. Thakur
Environmental Microbiology and Biotechnology Laboratory, School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, India

G. Saxena
Environmental Microbiology and Biotechnology Laboratory, School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, India

Department of Environmental Microbiology (DEM), Babasaheb Bhimrao Ambedkar (Central) University, Lucknow, Uttar Pradesh, India

Laboratory of Microbiology, Department of Microbiology, School of Life and Allied Sciences (SLAS), Baba Farid Institute of Technology (BFIT), Dehradun, Uttarakhand, India

M. P. Shah
Industrial Waste Water Research Laboratory, Division of Applied & Environmental Microbiology, Enviro Technology Limited, Ankleshwar, Gujarat, India

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_6

Thus, proper wastewater treatments are mandatory to remove contaminants before its discharge into the environment. Numerous physicochemical methods have been implemented for remediation or detoxification of distillery wastewater, which is viewed as a challenging job with respect to cost, technical complexity, and sludge generation in huge quantity with subsequent disposal problems. Therefore, there is an urgent need for safe management of hazardous distillery wastewater; the technologies must be economically viable, ecologically sound, and socially acceptable. This book chapter presents an overview of the generation of effluent, its chemical characteristics and environmental hazards. In addition, we have also discussed the existing treatment approaches and challenges for safe disposal of distillery wastewaer into the environment.

Keywords

Endocrine-disrupting chemicals · Melanoidins · Ligninolytic enzymes · Methanogenesis

6.1 Introduction

The worldwide demand for energy and the uncertainty of natural resources has led to the eco-friendly development of alternative liquid biofuels. Ethanol is one of the excellent candidates since it reduces dependence on fossil-fuel reserves. In developing countries like India, distilleries are one of the major agro-based polluting industries; in addition, they are a high consumer of fresh water and utilize the sugarcane molasses as the feedstock for ethanol making (Arimi et al. 2014; Kumar and Chandra 2018; Chandra and Kumar 2017a,b). However, there is serious environmental trouble with ethanol production from sugarcane molasses fermentation which is generally connected to the generation of dark brown-colored wastewater, known as a spent wash (SW) or raw wastewater/effluent (Kumar and Chandra 2018; Chandra and Kumar 2017a, b, c). It has been reported that SW produced from distilleries has a high organic load as compared to other raw material used for ethanol production (Kumar and Sharma 2019. There are three different organic wastes generated from the molasses based-distilleries which include yeast sludge, spent malt grain wash, and SW. A typical sugarcane molasses-based distillery generates 12–15 liters of SW for every liter of the ethanol produced. It stated that about 40.4 billion liters of SW are produced with a generation of 3.25 billion liters ethanol from 319 distilleries located in the tropical and subtropical region of India. SW is a dark brown-colored wastewater characterized by a specific obnoxious odor with high organic and inorganic load at acidic pH (Table 6.1). Wilkie et al. (2000) stated that COD is 4–5 times higher in sugarcane molasses-based SW as compared to sugarcane juice stillage. SW composition generally depends on the raw material used for sugar extraction as well as the distillation and fermentation processes adopted in distilleries for ethanol production. The dark brown-colored SW is one of the most obvious indicator of water and soil pollution. Apart from color, SW possesses a high

Table 6.1 Physicochemical characteristics of various types of waste generated by alcohol-producing molasses-based distilleries (Acharya et al. 2011; Mohana et al. (2007); Singh and Dikshit (2011) Chandra and Kumar (2017a, b)

Parameter	Spent wash	Anaerobically digested spent wash	Anaerobically digested spent wash sludge
Color appearance	Dark brown	Dark brown	Dark brown
Color intensity(co-Pt unit)	150,000	80,000	–
Odor	Like molasses	Unpleasant	–
pH	3.0–4.07	7.9–8.2	8.00–8.1
EC (μS cm^{-1})	–	33	2.29–4.12
Temperature (°C)	90	30	89
BOD (mg L^{-1}/mg kg^{-1})	40,000–60,000	8000–12,000	–
COD (mg L^{-1}/mg kg^{-1})	90,000–190,000	45,000–52,000	–
TS (mg L^{-1}/mg kg^{-1})	83,084–190,000	47,422–72,500	–
Sodium (mg L^{-1}/mg kg^{-1})	–		42.13–56.16
Chloride (mg L^{-1}/mg kg^{-1})	2200–8500	7842–7997	1272.74–1824.4
Phenol (mg L^{-1}/mg kg^{-1})	4.20–10,000	6893–7202	501.34
Sulfate (mg L^{-1}/mg kg^{-1})	5760–9000	180–3875	145.07
Phosphate (mg L^{-1}/mg kg^{-1})	5.36–2700	46–1625	2268.83
TN (mg L^{-1}/mg kg^{-1})	2800–7000	4096	2.468
TOC (mg L^{-1}/mg kg^{-1})	25,368	31,090	17.318
Reducing sugar (g%)	–	0.40–0.17	–
TVS	80,000–120,000		–
TSS (mg L^{-1}/mg kg^{-1})	13,000–15,000	29,810	–
TDS (mg L^{-1}/mg kg^{-1})	90,000–150,000	17,612	–
Ammoniacal nitrogen	–	2800	190
Trace elements			
Mn (mg L^{-1}/mg kg^{-1})	4.556	43.63	126.30–238.47
Cr (mg L^{-1}/mg kg^{-1})	1.05 ± 0.031	–	BDL-21.825
Zn (mg L^{-1}/mg kg^{-1})	BDL-2.487	1.24	43.47–210.15
Cu (mg L^{-1}/mg kg^{-1})	BDL-0.337	BDL-0.75	73.62–847.46
Fe (mg L^{-1}/mg kg^{-1})	163.947	57.50	2403–5264.49
Pb (mg L^{-1}/mg kg^{-1})	BDL	0.23	16.33
Cd (mg L^{-1}/mg kg^{-1})	BDL	1.30	BDL-1.440
Ni (mg L^{-1}/mg kg^{-1})	BDL-1.175	0.31	13.425–15.60

BOD biological oxygen demand, *COD* chemical oxygen demand, TS Total solids, TN Total nitrogen, *TSS* total suspended solids, *TS* total solids, *TDS* total dissolved solids, *TOC* total organic carbon, *TVS* total volatile solids, *EC* electrical conductivity, *Mn* Manganese, *Cr* Chromium, *Zn* Zinc, *Cu* Copper, *Fe* Iron, *Pb* Lead, *Cd* Cadmium, *Ni* Nickel, *BDL* Below detection limit concentration of reducing sugars, hemicelluloses, lignin, resins, dextrin, polysaccharides, organic acids, phenolic compounds, anthocyanins, tannins, fatty acids, sterols, and resins (Chandra and Kumar 2017a). High chemical oxygen demand (COD), biological oxygen demand (BOD), and persistent dark brown color of SW poses environmental, water, and soil pollution problems including a threat to plant and animal lives, and thus safe disposal of such kind of wastewater is challenging. In accordance with the environmental protection act and rules of the Ministry of Environment, Forests and Climate Change and Central Pollution Control Board (CPCB), Govt. of India, it is mandatory to treat hazardous SW before it is disposed into the environment. Indian government policies on pollution prevention have forced distilleries to look for an effective and sustainable technology for decreasing the SW characteristics. It is usually subjected to conventional aerobic and anaerobic secondary treatment approaches such as activated sludge, anaerobic digestion, and anaerobic lagoons processes, which easily remove organic matter (OM) and also reduce the BOD and COD of SW. However, these treatment methods do not decompose or decolorize melanoidins present in SW due to their recalcitrant nature and presence of other complex co-pollutants. Thus, adequate treatment is warranted before the wastewater is discharged into the environment. Hence, this book chapter is focused on the generation and characteristics of distillery wastewater (DW) pollutants, their environmental hazards as well as various existing physicochemical and biological treatment approaches used for DW. Further, the emerging treatment approaches used for DW have also been discussed.

6.2 Ethanol Manufacturing Process and Effluent Generation

Ethanol can be produced from various feedstock, including sugar-based materials (i.e., sugarcane juice and beet molasses), starch-based material (i.e., corn, barley, wheat, rice, and cassava), and cellulosic materials (i.e., crop residues and sugarcane bagasse). In India, distilleries used diluted sugarcane molasses (15–16%) as a chief feedstock material for ethanol production (7–8% v/v). In general, ethanol production consists of three steps: (i) feed preparation (fermentable sugar containing diluted molasses solution), (ii) fermentation (conversion of sugars to ethanol), and (iii) distillation (separation and purification of ethanol). For ethanol production, sugarcane molasses, and nitrogen and phosphate-containing food supplements are taken in a fermentation broth. Further, the fermentation process is carried out by yeast (*Saccharomyces cerevisiae*) culture, which converts the sugar into ethanol, and the yeast sludge settles down at the end of the process. The fermented mass contains 7–8% ethanol, which is separated in a distillation column as the top product, and brownish liquid as the bottom product known as SW (Fig. 6.1). In molasses-based distilleries, the fermentation process can be carried out by three modes; (i) batch, (ii) fed-batch, (iii) continuous mode. In a batch process, sugarcane molasses is diluted with water to reduce the sugar content from the existing 40–45% to 10–15%, and then yeast inoculum at about 10% concentration (v/v) is added with this diluted sugarcane molasses. Further, this diluted molasses is allowed to ferment for 30–40 hrs. After completion of fermentation, the yeast sludge is separate from the bottom of the

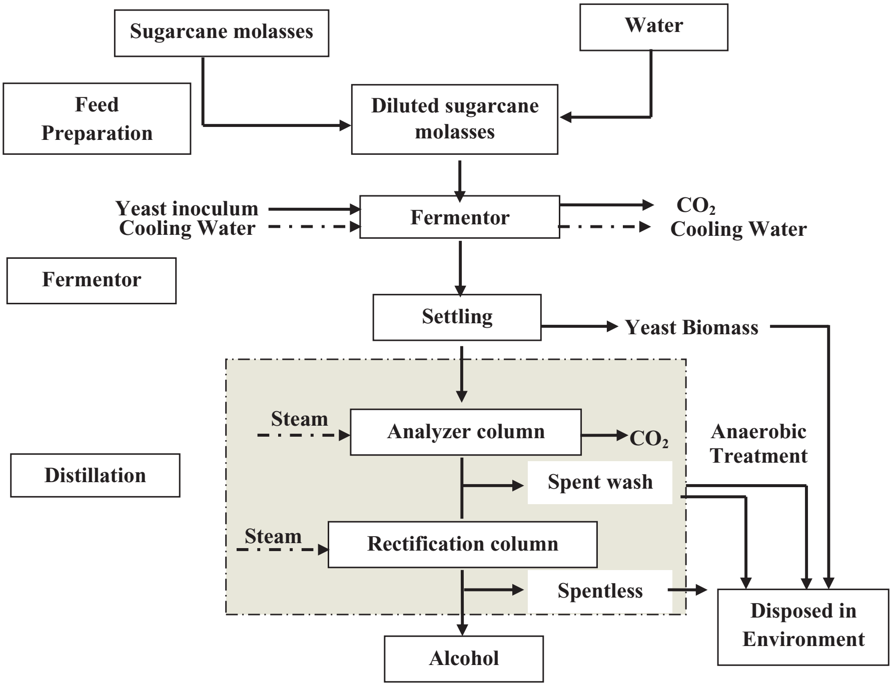


Fig. 6.1 Manufacture of ethanol from sugarcane molasses and generation of wastewater

fermenter (bioreactor) while the bioreactor wash is sent to the analyzer column for distillation with steam where a mixture of steam and ethanol vapors is collected at the top of the column and spent wash drained out from the bottom. The mixture of steam and ethanol is fed to the rectification column where rectified spirit (RS) is formed due to condensation of water and ethanol vapors. The condensed steam is discharged as spent lees (Fig. 6.1). In a fed-batch process, a combination of batch and a continuous mode, substrates (nutrients) are supplied (fed) to the bioreactor during cultivation and the product(s) remain in the bioreactor until the end of the run. Continuous mode is carried out by continually adding culture medium, substrates, and nutrients into a bioreactor containing microorganisms. During this process, the culture volume must be constant and the products formed after fermentation are continuously taken from the media. Absolute ethanol or fuel ethanol is generated by the dehydration of RS through molecular sieve technology where RS is passed through preheater to raise the temperature to 65 °C, then fed into the recovery column and heated through boiler by steam to produce alcohol vapors. Further, the alcohol vapors are superheated with steam and then passed through one of the pairs of molecular sieve beds in auto-mode. The water (H_2O) molecules are absorbed by the molecular sieves beds and become saturated within 5–6 min. When the first molecular sieve bed is saturated with H_2O, automatically ethanol vapors will pass through the second bed. The ethanol vapors having alcohol concentration of about 99.70% are condensed and stored in the collection tanks. The desorbed liquid contains 70–75% ethanol, which is partially used for creating a vacuum and remains recycled to the recovery column. During ethanol production, a huge amount of solid waste matter as a yeast sludge is formed in the distilleries, which cause pollution when it is disposed into the environment. Yeast sludge is rich in protein and contains a considerable amount of essential amino acids and drying sludge grains are marketed as livestock feed and make it the best source for the production of single cell protein. Generally, during ethanol production, distillery operations use water for various process and non-process applications. The process applications include preparation of sugarcane molasses for fermentation, yeast propagation, and steam requirements for distillation, while the non-process applications involve boiler water, wash water, cooling water used in making potable ethanol. The wastewaters discharged from the analyzer column, yeast sludge, spent less, water treatment plant, waste wash water, cooling water, boiler as blowdown, bottling plant, and other wastes as termed as SW. In distilleries, the major source of wastewater generation is the distillation step wherein a huge volume of dark brown-colored wastewater is generated. Average SW generation is highest in the batch process (11.1–15.0 liters per liter ethanol production), higher in the continuous process (8.5–11.0 liters per liter ethanol production), and lowest in the bio-still process (6–8 liters per liter ethanol production). Figure 6.1 illustrated the manufacturing process of ethanol from sugarcane molasses, along with the wastewater generation.

6.3 Distillery Wastewater: Nature and Chemical Characteristics

Over the last few decades, the occurrences of pollutants due to discharge of DW in the aquatic ecosystem and their toxic effects to human health as well as wildlife organisms have become major issues of increasing concern in India and other developing countries (Kumar and Sharma 2019). The majority of distilleries coexist with sugar mills and utilize sugarcane molasses as a starting material for ethanol production. In distilleries, a major fraction (~90%) of the fermented wash going to distillation column is discharged as SW (Chandra and Kumar 2017b). The characteristics of SW vary significantly according to the fermentation feedstock, and the fermentation/distillation processes adopted. SW is characterized with unpleasant odor; deep brown color; high level of BOD, COD, TDS, total solids (TS), total nitrogen (TN) sulfate and phosphate; and the presence of various heavy metals (HMs) ions such as iron (Fe^{3+}), zinc (Zn^{2+}), copper (Cu^{2+}), nickel (Ni), manganese (Mn^{2+}), and lead (Pb^{2+}) and numerous endocrine-disrutping chemical (EDCs) (Tables 6.1 and 6.2).

The high organic load of SW is primarily composed of melanoidins (Maillard reaction products; MRPs), thermal degradation products (hexose alkaline degradation products; HADP), and sugar condensation reaction products (overheated sugars; caramels) (Hatano et al. 2013; Hatano and Yamatsu 2018; Kumar and Chandra 2018). The MRPs formed through the nonenzymatic browning reaction also known as Maillard reaction occurs between amino acids and reducing sugars and caramels at elevated temperatures that are responsible for deep brown color and odor in the SW (Kumar and Chandra 2018, 2020). Besides, the color of SW is also generally attributed to the existence of a wide variety of naturally polymeric colorants such as

Table 6.2 Organic pollutants identified by gas chromatography-mass spectrometry (GC-MS) technique in (a) acetone (b) ethyl acetate (c) isopropanol (d) methanol (e) ethanol and (f) n-hexane extracted sample of distillery spent wash (Chandra and Kumar 2017a, b, c)

SI. No.	Retention time	Identified compounds
(a)		
1.	8.66	1,3-Propanediol, TMS ether
2.	9.88	Propanoic acid, 3-[(TMS)oxy)-TMS ether
3.	10.27	Butanoic acid, 3-methyl-2-[(TMS)oxy]-TMS ether
4.	11.54	D-Erythrotetrofuranose, tris –O-(TMS)
5.	11.87	Pentanoic acid
6.	13.78	Butanedioic acid, bis(TMS) ester
7.	15.52	Resorcinol, O-bis(TMS)
8.	16.01	2,3-Butandiol, bis-O-(TMS)
9.	17.34	Malic acid (O-(trimethylsilyl)-bis(trimethylsilyl ester)
10.	17.54	2-Methyl-1,3-Butanediol 2TMS
11.	19.60	2-Furancarboxylic acid, 5-[[(TMS) oxy] methyl], TMS ester
12.	20.19	2,3,5-tri-O- TMS-arabino-1,5-lactone
13.	22.18	Cyclooctene, 1,2-bis(trimthylsiloxy)
14.	22.15	Tricarballylic acid TMS
15.	22.81	D-ribo-Hexanoic acid, 3-deoxy-2,56, tris-O-(TMS), lactone
16.	23.54	Benzoic acid, 3,4-bis [(TMS)oxy], TMS ester
17.	24.19	Tert-butylhydroquinone, bis (TMS) ether
18.	24.87	Trimethylsilyl 3,5-dimethoxy-4-9 TMS oxy)benzoate
19.	26.48	Vanillypropionic acid, bis (TMS)
20.	30.61	Benzeneacetic acid, α,4-bis[(TMS) oxy]-methyl ester
(b)		
1.	8.23	L-lactic acid, TMS ether, TMS ester
2.	8.48	Acetic acid, [(TMS)oxy], TMS ester
3.	10.33	Butanoic acid, 3-methyl-2-[(TMS), TMS ester
4.	10.70	Valeric acid, 5-methoxy, TMS ester
5.	11.86	2-Hydroxysocaproic acid, TMS ether,
6.	12.24	Ethyl(TMS) succinate
7.	12.90	1,3-Propanediol, TMS ether
8.	13.78	Butanedioic acid, bis(TMS)ester
9.	13.94	Diethyl methylsuccinate
10.	15.22	Lactic acid dimer, bis(TMS)
11.	16.00	Silane, [1,4-phenylenebis(oxy)]bis(trimethyl)
12.	16.56	2-Methyl-1,3Propanediol 2TMS
13.	18.59	2-Furancarboxylic acid, 5 -[[(trimethylsilyl)oxy] methyl], TMS ester
14.	19.18	Benzenepropanoic acid, α-[(TMS)oxy], TMS ester
15.	20.09	Benzoic acid, 4-[(TMS)oxy], TMS ester
16.	20.25	Ethyl-TMS dipropylmalonate
17.	20.62	Bicyclo[4.3.0]nonane −2-one,[Z]-cis-8-(phenyl-1-trimethylsilylmethylene)

(continued)

Table 6.2 (continued)

SI. No.	Retention time	Identified compounds
18.	20.98	2-Hydroxyheptanoic acid 2TMS
19.	21.32	D-erythro-Hex-2-enoic acid, 2,3,-di-O-methyl-5,6-bisO-(TMS)-ϒ-lactone
20.	22.23	Tricarballylic acid 3TMS
21.	22.65	Benzoic acid, 3-methoxy-4-[(TMS)oxy], TMS ester
22.	24.89	Trimethylsilyl 3,5 dimethoxy-4-(TMS oxy)benzoate
23.	25.96	3-Vanil-1,2-Propanediol 3TMS
24.	27.01	B-D-Galactopyranoside, methyl 2,6-bis-O-(TMS)-cyclic butyboronate
25.	27.83	Silane, (preg-5-ene-3β,11β,17,20β-tetraylteraoxy) tetrakis (trimethyl)
(c)		
1.	8.49	Propanoic acid, 2–9 (TMS)oxy],- TMS ester
2.	13.75	Butanedioic acid, bis(TMS)ester
3.	15.32	Butane, 1,2,4-tris (trimethylsilyloxy)
4.	16.01	2-Methyl-1,3-Propanediol- 2- TMS
(d)		
1.	10.14	Propanoic acid, 3-[(TMS)oxy], TMS ester
2.	10.44	Butanoic acid, 3-methyl-2-[(TMS)oxy], TMS ester
3.	10.93	2-Methylbutanoic acid, 3-(t-butlydimethylsilyloxy),-methyl ester
4.	11.71	Erythro-pentitol, 2-dedoxy-1,3,4,5-tetrakis-O-(TMS)
5.	16.04	3,6-Didoxa-2,7-Disilaoctane, 2,2,4,5,7,7-Hexamethyl
6.	19.95	Cyclooctene, 1,2-bis-(trimethylsilyloxy)
7.	20.22	2,3,5,-tri-O-trimethylsily-arabino-1,5-lactone
8.	22.85	D-ribo-hexanoic acid, 3-deoxy-2,5,6 tris-O-(TMS)-lactone
(e)		
1.	8.48	D-lactic acid-Di TMS
2.	12.39	Ethyl (trimethyl)succinate
3.	13.76	Butanedioic acid, bis (TMS)ester
4.	16.03	3,6-Dioxa-2,7-disilaoctane,2,2,4,7,7-pentamethyl
5.	17.77	Erytritol per-TMS
6.	20.21	2,3,4,5-tetrahydroxypentanoic acid-1,4-lactone, tris (TMS)
7.	21.07	Cyclooctene, 1,2-bis(trimethylsiloxy)
8.	22.76	D-Ribo-Hexanoic acid, 3-deoxy-2,5,6-tris-O-(TMS) lactone
9.	23.12	α-D-Galactopyranose, 1,2,3-tris-O-(TMS), cyclic methylboronate
(f)		
1.	12.31	Benzene, 1-ethyl-3,5-disopropyl
2.	12.87	Eicosane
3.	35.69	3,4-Dihyroxymandelic acid, ethyl ester, tri-TMS
4.	36.56	Octadecane,3-ethyl-5(2-ethylbutyl)
5.	37.57	Celidonil, Deoxy

carotenoids, chlorophyll, resins, fatty acids, heme pigment, anthocyanins, tannins, riboflavin, betalains, quinone pigments, polyphenols, melanin, and metal sulfides (Borja et al. 1993; Arimi et al. 2014; Pant and Adholeya 2007). Among these colorants, melanoidins are major nitrogenous, high molecular weight (5–40 kDa), polymeric, acidic, negatively charged imparting organic compounds present at high concentration in SW. Melanoidins are toxic to microorganisms and recalcitrance to biological wastewater treatments; therefore, DW must be treated before disposal into the environment. It has been demonstrated that various HMs such as Mn^{2+}, Co^{2+}, Zn^{2+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, and Fe^{3+} bind with melanoidins to make an organometallic complex and, consequently, enhance the toxicity of SW into the environment (Hatano et al. 2016; Migo et al. 1997; Chandra et al. 2018a, b, c, d). Polyphenols and melanoidins may also be the source of the formation of aromatic halogenated disinfection by-products (DBPs) during chlorine disinfection of DW. Liu and Zhang 2014 reported that aromatic halogenated DBPs showed higher developmental toxicity and growth inhibition than aliphatic halogenated DBPs. However, the colloidal nature of caramels makes the SW resistant to biological degradation and toxic to aquatic and terrestrial organisms. The obnoxious odor of DW mainly occurs due to the presence of indole, skatole, and other sulfur compounds. In addition, some toxic chemicals such as tricarballylic acid 3TMS; benzoic acid 3-methoxy-4-[(TMS)oxy], TMS ester; benzenepropanoic acid; α-[(TMS)oxy], TMS ester; 2-furancarboxylic acid, 5-[[(TMS)oxy] methyl], TMS ester; vanillylpropionic acid, bis(TMS); 2-hydroxysocaproic acid; and butanedioic acid bis(TMS) ester are also present in SW (Yadav and Chandra 2012). These organic compounds are well reported as potential EDCs by the US Environmental Protection Agency (USEPA) (2012). Hence, due to its toxic nature, SW must be treated properly before it is disposed into the environment (Tewari et al. 2007). In order to lower the high BOD and COD level, presently many distilleries are recycling this wastewater for getting fuel in the form of methane (Joshi et al. 1994). SW received after anaerobic digestion is called post-methanated distillery effluent (PMDE) or biomethanated distillery effluent (BMDE), which contains a higher level of BOD, COD, TDS, and phenols, with dark brown color, strong odor, and alkaline pH. Besides organic content, BMDE also contains a high level of nitrogen, potassium, sulfur, and phosphorus, which can lead to eutrophication of aquatic ecosystem. In addition, BMDE retains a high amount of various HMs (Table 6.1). This means that SW after anaerobic digestion retains high organic and inorganic load and it is not safe for discharge into the environment (Chandra et al. 2018a; Kaushik and Thankur 2009). Besides the effluent, sugarcane molasses-based distilleries produce huge amount of anaerobically digested SW sludge which has been reported for high concentration of phenolics, melanoidins, and complex OM along with metallic ions (i.e., Cd^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}, Pb^{2+}, Ni^{2+} and Zn^{2+}) and nonmetallic ionic compounds (i.e., Na^{+}, Cl^{-}, $SO_2{}^{-4}$, $PO_3{}^{-4}$) (Table 6.1). Recently, distillery sludge is reported to contain high amount of plant-derived hexadecanoic acid; octadecanoic acid; n-pentadecanoic acid; stigmasterol; β-sitosterol trimethyl ether; heptacosane, lanosta-8, 24-dien-3-one, 1-phenyl-1-propanol, and 1-methylene-3-methyl butanol; dotriacontane; dodecanoic acid; 2-ethylthio-10-hydroxy-9-methoxy-1,4 anthraquinone; 5α-cholestane, 4-methylene; and campesterol TMS as potential

EDCs reported by the USEPA (Chandra and Kumar 2017a, c; Chandra et al. 2018b). All these features combined with the huge volume of DW and sludge disposed of distilleries causes important environmental issues. Therefore, the elimination and biodegradation of organic and inorganic toxic compounds are necessary for the safe disposal of DW into the environment.

6.4 Environmental Pollution and Toxicity Profile of Distillery Wastewater

Distilleries generate a huge volume of wastewater during ethanol production, and most of the distilleries dispose their partially treated or untreated wastewater into water bodies causing environmental threats to organisms. Due to high pollution nature of DW, MoEF listed alcohol industries at the top among the "Red category" industries (Tewari et al. 2007). Regarding environmental pollution, the government of India made rules and regulations in 1976 and again revised them in 1983. The Bureau of Indian Standards (BIS) provides guidelines to state and central government authorities which would help to decide boundaries on effluent disposal and to the industry for selecting effective technology and the degree of treatment required for DW before their disposal. In an aquatic ecosystem, the DW reduced penetration of sunlight in lagoons, lakes, and rivers, which in turn decreases both dissolved oxygen and photosynthetic activity, thereby aquatic life suffers, resulting in deterioration of water quality and loss of productivity to such an extent that the water becomes unusable (Kumar and Gopal 2001; Chandralata et al. 2004; Ramakritinan et al. 2005; Kumar and Chandra 2006; Kumar and Sharma 2019). Disposal of DW on land is equally hazardous; it inhibits germination of seeds and depletes vegetation by decreasing the soil alkalinity, salinity, and manganese availability (Jadhav and Savant 1975; Chandraju and Basavaraju 2007; Bharagava and Chandra 2010; Narain et al. 2012; Srivastava and Jai 2010; Arora et al. 1992; Kannan and Upreti 2008). Chandra and Kumar (2017b) reported the toxic effects of SW at different concentrations on seedling growth of *P. mungo* L. and *T. aestivum*. In a another study, Chandra and Kumar (2017a) also reported the presence of androgenic-mutagenic compounds and potential autochthonous bacterial communities during in situ bioremediation of anaerobically digested distillery sludge and also tested the toxicity of in situ degraded sludge leachate by using *Allium cepa* L. root meristematic cell. They showed a reduction of toxicity in degraded samples of sludge and leachate, confirming the role of autochthonous bacterial communities in the bioremediation of distillery waste in situ. Nonjudicious use of PMDE adversely affected crop growth and decreased physicochemical properties (Jagdale and Sawant 1975; Joshi et al. 2000; Tripathi et al. 2011). However, the judicious application of PMDE improved crop productivity and alleviated environmental pollution problems (Devarajan et al. 1994; Davamani et al. 2006). The impact of distillery waste on the environment and their eco-friendly and advanced cleaner technologies used to combat the threat are illustares in Fig. 6.2.

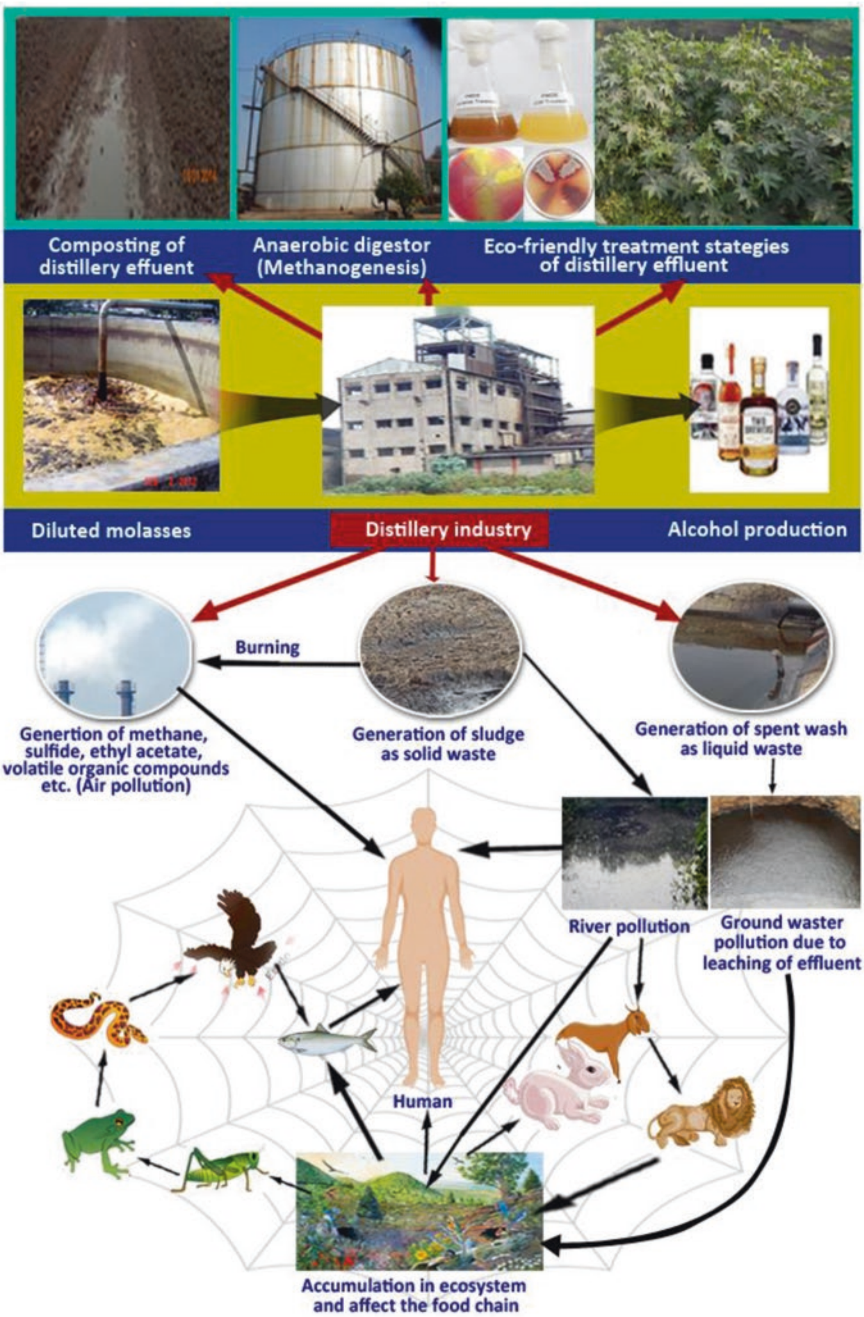


Fig. 6.2 Discharged distillery waste and its environmental impact and treatment technologies to combat the threat

6.5 Treatment Approaches for Distillery Wastewater

DW is a major threat to the environment, and it is therefore essential to adequately treat the DW prior to its safe disposal into the environment. This can be achieved by using biological, physical, and chemical approaches, either alone or in combination (Fig. 6.3).

6.5.1 Biological Treatment Approaches

Biological approaches have been recognized as eco-friendly and most effective methods for the treatment of highly polluted DW whereby organic substances are used as food by growing microorganisms such as bacteria, fungi, yeast, and cyanobacteria. The end result is a decrease in the number of organic pollutants and an increase in the number of microorganisms, carbon dioxide (CO_2), water (H_2O), and other by-products of microbial metabolism (Kumar et al. 2018; Kumar and Chandra

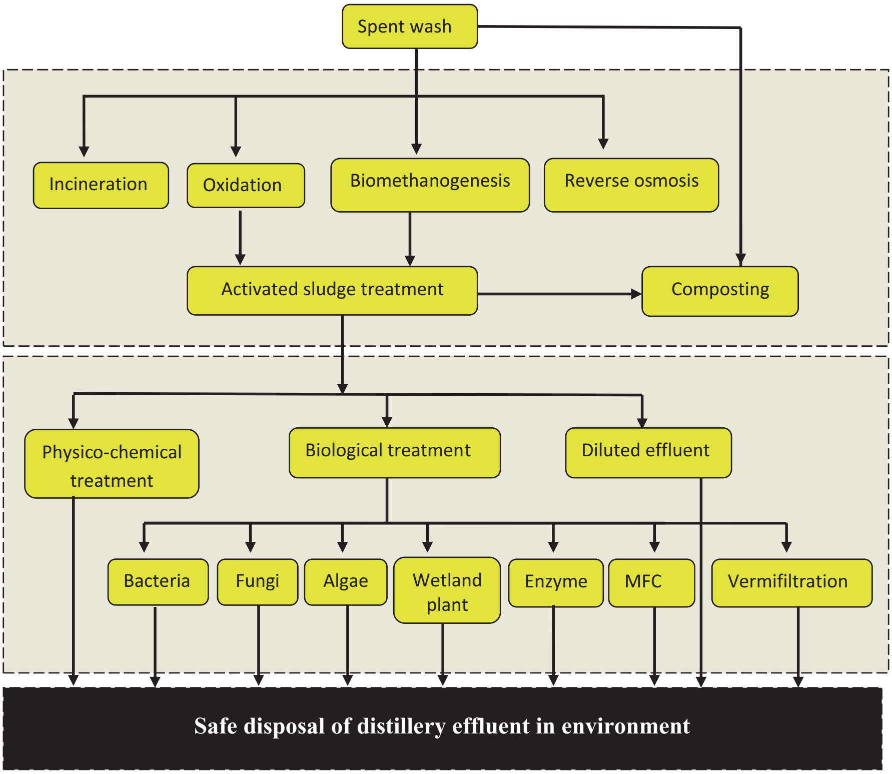


Fig. 6.3 Different physicochemical and biological approaches used for treatment of distillery wastewater

2020. The role of anaerobic and aerobic biological treatment approches in DW treatment are discussed in the following sections.

6.5.1.1 Anaerobic Treatment

Distillery SW retains high BOD/COD ratio (1.11–1.25), TDS, and high concentration of inorganic solids with low pH and high temperature. In order to decrease its high COD and BOD level, presently many distilleries are recycling this effluent for getting fuel in the form of methane (CH_4) through anaerobic digestion (AD). AD is a multifaceted treatment process requiring the potential activity of different group of microorganisms interacting in a bioreactor. The breakdown of OM in an anaerobic reactor typically involves four major degradation phases: (i) hydrolysis, (ii) acetogenesis, (iii) acidogenesis, and (iv) methanogenesis. In the first three phases, organic pollutants are hydrolyzed and/or fermented into intermediate short-chain fatty acids which are further degraded to acetate and hydrogen and carbon dioxide. Further, in the fourth phase, acetate and H_2/CO_2 are converted into methane. Anaerobic treatment is a broadly accepted an effective exercise, and different high-rate anaerobic reactor designs have been tried for DW treatment. One of the methods that are used to treat DW is the application of upflow anaerobic sludge blanket (UASB) reactor. The UASB process is an attractive treatment because of low cost, high treatment efficiency, biogas generation, and ability to handle high organic loading rates (OLRs) and requires shorter hydraulic retention time (HRT) than other reactors (Keyser et al. 2003; Acharya et al. 2008). The UASB reactor has four major components, i.e., sludge bed, sludge blanket, gas-solid separator, and settlement compartment. A two-stage process with an anaerobic filter followed by a UASB reactor was investigated by Blonskaja et al. (2003). The acidogenic and methanogenic phases were clearly separated ensuring better conditions for the methanogens. COD reduction was 54% and 93% in the first and second stage, respectively. Table 6.3 provides a summary of different reactor configurations used for the anaerobic digestion of SW. The limitations of anaerobic treatment processes are the requirement of high dilution due to the presence of many antimicrobial compounds (Bharagava and Chandra 2010). AD can remove a substantial amount of organic load when applied in treating DW, but it is ineffective in color reduction and several recalcitrant pollutants. Therefore, further treatment is required to remove the remaining dark color and COD, BOD, etc. However, researchers have reported various alternatives for further treatment of BMDE through aerobic route and resource the recovery.

6.5.1.2 Aerobic Treatment

Aerobic processes are usually applied as post-aerobic treatment of BMDE, based on pollutant degradation by the utilization of specific microorganisms, either as pure strains or as a consortium. These processes generally depend on the oxidative activities of microorganisms, viz., fungi, yeast, bacteria, and cyanobacteria, used by the various researchers for the treatment of raw SW as well as BMDE in the presence of oxygen (Chandra and Kumar 2015a).

Table 6.3 Performance efficiency of various anaerobic reactors used for the treatment of spent wash

	Reduction %			
Reactor	BOD	COD	HRT	References
Upflow anaerobic fixed film bioreactor	–	64	–	Acharya et al. (2008)
Bench-scale UASB reactor	95	69	–	López et al. (2018)
Expanded granular sludge bed reactors	–	80–90	–	López et al. (2018)
Thermophilic UASB reactor	>80	39–67	–	Harada et al. (1996)
UASB reactor	–	83.87	24 hrs	Thiyagu and Sivarajan (2018)
Anoxic-aerobic ultrafiltration membrane bioreactors	–	93	20–39 hrs	Wolmarans and de Villiers (2002)
UASB reactor	84–89	72–91	20 hrs	Saini and Lohchab (2017)
UASB reactor	–	90–95	–	Moletta (2005)
Anaerobic filter and UASB reactor	–	90	1.3 days	Blonskaja et al. (2003)
Anaerobic granular sludge reactor	–	80–90	1 day	Collins et al. (2005)
Anaerobic filter followed by a UASB reactor	–	54 and 93		Blonskaja et al. (2003)
Downflow fixed-film reactor	60–73	85–97	3.3–2.5 days	Bories et al. (1988)
UASB reactor	89.11	68.35	2 days	Saner et al. (2014)

BOD biological oxygen demand, *COD* chemical oxygen demand, *HRT* hydraulic retention time, *UASB* upflow anaerobic sludge blanket, *hrs*, hours

6.5.1.2.1 Fungal Treatment

In the last two decades, the fungi species belonging to basidiomycetes and ascomycetes class have been used in the decolorization of natural and synthetic melanoidins in connection with the color reduction of DW. The aim of fungal treatment is to reduce the COD and BOD of DW and at the same time to obtain some valuable products, such as fungal biomass for protein-rich animal feed, extracellular organic acids, or some specific fungal metabolites. Several fungi species such as *Geotrichum candidum* (Kim and Shoda 1999), *Trametes* sp. (Gonzalez et al. 2000), *Coriolus hirsutus* (Miyata et al. 2000), *Flavadon flavus* (Raghukumar and Rivonkar 2001), *A. niveus* (Angayarkani et al. 2003), *Phanerochaete chrysosporium* (Dhaiya et al. 2001; Thakkar et al. 2006), *Pleurotus florida, Aspergillus flavus* (Pant and Adholeya 2009a), *Neurospora intermedia* (Kaushik and Thakur 2013), *Fusarium verticillioides* (Pant and Adholeya 2009b) and yeast *Citeromyces* sp., *Candida tropicalis* (Tiwari et al. 2012), and *Candida glabrate* (Mahgoub et al. 2016) have been reported for the degradation and decolourisation of melanoidins containing DW. A list of yeast and fungi species used by various researchers for decolorization and degradation of DW is given in Table 6.4. The degradation and decolorization of melanoidins by fungus have occurred due to the prevalence of ligninolytic enzymes, i.e.,

Table 6.4 Various yeast and fungi species capable for COD, BOD reduction and decolorization of distillery wastewater

Microorganisms	Incubation time	Reduction %			References
		Decolorization	BOD	COD	
Yeast	2–5 days	60.00	–	–	Mahgoub et al. (2016)
Candida tropicalis RG-9	24 hrs	75.00	–	–	Tiwari et al. (2012)
Issatchenkia orientalis	7 days	60.00	–	–	Tondee and Sirianutapiboon (2008)
Fungi					
Trametes sp. I-62	7 days	73.30	–	61.70	Gonzalez et al. (2000)
Emericella nidulans var. lata (DF3)	–	38.00	–	–	Kaushik and Thakur (2009)
Neurospora intermedia (DF4)	–	31.00	–	–	Kaushik and Thakur (2009)
Phanerochaete chrysosporium	10 days	85.00	–	–	Fahy et al. (1997)
Aspergillus oryzae MTCC 7691	–	75.71	51.00	86.19	Chavan et al. (2013)
Geotrichum candidum Dec 1	–	80.00	–	–	Kim and Shoda (1999)
Cladosporium cladosporioides	–	62.50	–	73.60	Ravikumar et al. (2013, 2011)
Flavodon flavus (Klotzsch) Ryvarden	8 days	80.00	–	–	Raghukumar and Rivonkar (2001)
Penicillium pinophilum TERI DB1	–	50.00	–	–	Pant and Adholeya (2007)
Alternaria gaisen TERI DB6	–	47.00	–	–	Pant and Adholeya (2007)
Penicillium florida EM 1303	–	86.00	–	–	Pant and Adholeya (2007)
Phanerochaete chrysosporium JAG-40	6 days	80.00	–	–	Dahiya et al. (2001)
Coriolus versicolor	–	71.5	–	90.00	Kumar et al. (1998)
Aspergillus species	–	–	–	–	Wagh and Nemade (2018)
Aspergillus nidulans Var. nidulans	7 days	79.6	–	62.00	Adikane and Patale (2014)
Stenotrophomonas maltophilia	–	–	–	–	Thiyagu and Sivarajan (2018)
Aspergillus niveus	–	56.00	94.00	97.14	Angayarkanni et al. (2003)
Coriolus versicolor Ps4a	4	75.00	–	–	Aoshima et al. (1985)
Neurospora intermedia,	–	–	–	–	Kaushik and Thakur (2009)
Emericella nidulans var. lata	–	–	–	–	Kaushik and Thakur (2009)
Aspergillus fumigatus	–	–	–	–	Mohammad et al. (2006)

BOD biological oxygen demand, *COD* chemical oxygen demand, *hrs Hours* manganese peroxidase (MnP), laccase (Lac), and lignin peroxidase (LiP), which metabolize melanoidins and other refractory organic compounds present in the DW as sole carbon and nitrogen sources (Miyata et al. 2000; Bonugli-Santos et al. 2012; Pant and Adholeya 2007, 2009a, b). The Lac and MnP have a broad range of substrate oxidizing enzymes able to cleave large varieties of several chemical bonds present in phenolic and nonphenolic recalcitrant compounds (Wong 2009). Miyata et al. (1998) demonstrated that synthetic melanoidin is decolorized by the sharing of manganese-dependent and -independent peroxidases of *Trametes* (*Coriolus*) *hirsutus* pellets, and the extracellular H_2O_2 along with the participation of Lac enzyme. MnP and Lac protein both act on pollutants in synergy resulting in the degradation and depolymerization of melanoidins (Miyata et al. 2000; González et al. 2008). González et al. 2008 and Miyata et al. (2000) have demonstrated that the presence of melanoidins and other similar compounds can induce the expression of MnP and Lac genes. González et al. (2008) report the induction of Lac by molasses wastewaters and molasses melanoidins in the *Trametes* sp. I-62. Tapia-Tussell et al. (2015) also reported the expression of Lac genes in the *T. hirsutus* strain Bm-2, in the presence of phenolic compounds, as well as its effectiveness in removing colorants from vinasse. In the presence of all phenolic compounds (i.e., guaiacol), increased levels of laccase-encoding mRNA were 40 times higher than those in the control. So far ligninolytic enzymes have been known to be produced by various fungi, but most of them have failed to bring about complete mineralization of melanoidins and other organic pollutants present in DW. However, the long growth cycle; long hydraulic retention time, requiring nitrogen limiting conditions; and low pH range (3.0–5.0) for complete decolorization of DW still limit the performance of the fungal decolorization system.

6.5.1.2.2 Bacterial Treatment

Bacterial cultures have a very high potential for biodegradation and decolorization of DW due to their higher environmental adaptability, faster growth rate, and high metabolizing capability of melanoidins. Thus, the degradation and decolourisation of synthetic and natural melanoidins was reported by various researchers using the axenic and mixed bacterial consortium. Pioneering work on SW decolorization by bacteria was done by Kumar et al. (1997). They observed that two aerobic bacterial isolates LA-1 and D-2 brought about maximum decolorization (36.5% and 32.5%) and COD reduction (41% and 39%) under optimized conditions in eight days. Various bacterial groups, such as *Bacillus* sp. (Kambe et al. (1999*), Pseudomonas putida, Aeromonas* sp. (Ghosh et al. 2002), *Lactobacillus plantarum* (Tondee and Sirianutapiboon 2008), *Alcaligenes faecalis* (Santal et al. 2011), *Pseudomonas* sp. (Sankaran et al. 2015), *Bacillus* sp. (Krzywonos 2012), and *B. badius* (Mehta et al. 2014), have been reported for the degradation and decolorization of melanoidin-containing DW. Some of the bacterial species investigated for their ability for decolorization and degradation of DW are summarized in Table 6.5. Bacterial decolorization is promising and faster compared to fungal decolorization, but an individual bacterial strain usually cannot degrade melanoidins completely, and the metabolites are often more toxic compared to parental compounds, which need to

Table 6.5 Bacterial species capable of COD, BOD reduction and decolorization of distillery wastewater

Microorganisms	Incubation times	Decolorization	Reduction % BOD	Reduction % COD	References
Pure bacterial isolates					
Paracoccus pantotrophus	5–6 days	–	–	81.2	Santal et al. (2016)
Pseudomonas sp.		26.08	–	–	Sankaran et al. (2015)
Alcaligenes faecalis SAG_5	5 days	72.6	–	–	
Pseudomonas aeruginosa		92.77	–	–	Charles et al. (2015)
Bacillus subtillis	24 hrs	85.00	–	–	Tiwari et al. (2012b)
Lactobacillus plantarum no. PV71–1861	7 days	68.12	–	–	Tondee and Sirianutapiboon (2008)
Lactobacillus plantarum		44.00	–	–	Krzywonos and Seruga (2012)
Acetogenic bacteria BP103	5 days	72.00	58.50	82.20	Sirianuntapiboon et al. (2004)
Bacterial consortium					
Proteus mirabilis, *Bacillus* sp., *Raoultella planticola* and *Enterobacter sakazakii*	10 days	75.00	–	71.00	Yadav and Chandra (2012)
B. licheniformis Bacillus sp. and *Alcaligenes* sp.		70.00	–	–	Bharagava and Chandra (2010)
Klebsiella pneumoniae, Salmonella enteric, Enterobacter aerogenes, and *Enterobacter cloacae*	168 hrs		25.51	53.43	Kumar and Chandra (2018); Chandra et al. (2018a)
Acinetobacter sp., Pseudomonas sp., *Comamonas* sp., *Klebsiella oxytoca, Serratia marcescens*, and *unidentified bacteria*	48 hrs	26.50	–	–	Jiranuntipona et al. (2009)
Pediococcus acidilactici and *Candida tropicalis*	24 hrs	82.15	–	–	Tiwari et al. (2014)

(continued)

Table 6.5 (continued)

Microorganisms	Incubation times	Decolorization	Reduction % BOD	 COD	References
Pseudomonas aeruginosa PAO1, *Stenotrophomonas maltophila*, and *Proteus mirabilis*	24 hrs	67.00	–	51	Mohana et al. (2007)
Bacillus (C1 and C2)					Krzywonos (2012)
Bacterial communities					
Microbacterium hydrocarbonoxydans, Achromobacter xylosoxidans, Bacillus subtilis, B. megaterium, B. anthracis, B. licheniformis, A. xylosoxidans, Achromobacter sp.*, B. thuringiensis, B. licheniformis, B. subtilis, Staphylococcus epidermidis, Pseudomonas migulae, Alcaligens faecalis, B. cereus*	30 days	75.50	–	85–86	Chaturvedi et al. (2006)
Pseudomonas, Enterobacter, Aeromonas, Stenotrophomonas, Acinetobacter, and *Klebsiella* sp.		44.00	–		Ghosh et al. (2004)

BOD biological oxygen demand, *COD* chemical oxygen demand, *hrs* hours

be further decomposed. Therefore, the utilization of bacterial consortia offers significant advantages over the use of pure bacterial cultures in degradation and decolorization of melanoidins, as different bacterial strains may attack the melanoidin molecules at different positions or may use decomposition products produced by another strain for further decomposition. Various biological studies have been earlier carried out by a number of researchers using bacterial consortium that included *Pseudomonas aeruginosa*, *Stenotrophomonas maltophilia*, *Proteus mirabilis* (Mohana et al. 2007), *Klebsiella oxytoca*, *Serratia marcescens*, *Citrobacter* sp., (Jiranuntipon et al. 2008), *B. licheniformis*, *Bacillus* sp., *Alcaligenes* sp. (Bharagava et al. 2009), and *Proteus mirabilis*, *Bacillus* sp., *Raoultella planticola*, and *Enterobacter sakazakii* (Yadav and Chandra 2012) to treat DW. In recent years, the ligninolytic system of bacteria with respect to their enzymatic potential for the bioremediation degradation of synthetic melanoidins and BMDE pollutants has been extensively studied (Pant and Adholeya 2009b). LiP, MnP, and Lac are the three major lignin-degrading enzymes with great potential in industrial applications (D'Souza et al. 2006). Out of the three, mainly Lac and MnP play a major role in the degradation of melanoidins (Kumar and Chandra 2018). Chandra and Kumar (2018) reported that MnP is profusely present at the initial phase of bacterial growth, while laccase was produced in a later phase of growth during melanoidin degradation and decolorization.

6.5.1.2.3 Cyanobacteria/Algal Treatment

Cyanobacteria are prokaryotic, gram-negative, photoautotrophic eubacteria having the ability to take up their nutrients from DW as sole carbon and nitrogen source, and thereby decolorizing the wastewater resulting in the reduction of color, BOD, and COD. Another advantage of using cyanobacteria is that, apart from the degradation of the melanoidin, it also oxygenates water bodies thereby reducing the energy need of the aerobic treatment. Kalavathi et al. (2001) reported degradation and decolorization of melanoidin in DW by the *Oscillatoria boryana* BDU 92181. This marine cyanobacterium degrades melanoidins due to the production of hydrogen peroxide, perhydroxyl, hydroxyl, and active oxygen radicals, resulting in the 60% decolorization of the DW. They further identified enzymes from microalgae, namely, glucose oxidase, MnP, and two MIP, involved in maximum production of hydrogen peroxide. In addition, riboflavin, manganese sulfate, methyl viologen, reduced glutathionine, and ascorbic acid could be used by *O. boryana* BDU 92181 for improving the degradation rate of melanoidins. A study conducted by Patel et al. (2001) examined the 26%, 81%, and 96% decolorization of DW through bioflocculation by *Synechocystis* sp., *Lyngbya* sp., and *Oscillatoria* sp., respectively. Valderrama et al. (2002) used a combined treatment of *Lemna minuscule* and *Chlorella vulgaris* for color removal from DW. They reported 52% color removal from DW by this combined treatment. Solovchenko et al. (2014) have investigated the possibilities of DW bioremediation along with a new *C. sorokiniana* sp. cultivated in a semi-batch mode in a high-density photobioreactor. A decrease in COD of the DW from 20,000 to ca. 1500 mg L^{-1} was achieved over 4 days with a decline in nitrate (>95%), phosphate (77%), and sulfate (35%). Recently, Krishnamoorthy et al. (2017) have shown the treatment of anaerobically digested DW with *Oscillatoria* sp. This organism reduced COD up to 55% of anaerobically digested DW. Although biological methods provide an eco-friendly approach for DW treatment, these methods also have some technical difficulties as far as in situ administration of pollutant is concerned.

6.5.1.2.4 Phytoremediation Approaches

Phytoremediation is an in situ, cost-effective, and eco-friendly technique to eliminate hazardous HMs and organic pollutants from the contaminated environment (Chandra et al. 2015, Chandra and Kumar 2018; Chandra et al. 2018b, c, d). It is an emergent green technology that employs plants and their associated microbiota to remove, reduce, immobilize, and/or degrade harmful environmental pollutants (Ma et al. 2011; Glick 2010). This can reduce the health risk from contaminated water, sediments, sludge, and soil through contaminant degradation or removal (Chandra and Kumar 2015b; Alkorta et al. 2004; Rajkumar and Freitas 2008). For the removal of DW contaminants, there is some significant work done by Billore et al. (2001) for a horizontal flow gravel bed constructed wetland (CW) to treat DW. After secondary conventional treatment, the concentrations of COD and BOD_5 in DW amounted to 2540 and 13,866 mg L^{-1}, respectively, and, therefore additional treatment was essential. The CW treatment system achieved BOD_5, COD, total P, and, total Kjeldahl nitrogen (TKN) reductions up to 84%, 64%, 79%, and 59%. This study recommended that CW may be a sustainable tertiary treatment technique for the remediation of contaminants present in DW. Similarly, Trivedy and Nakate (2000) used wetland plant *T. latipholia* for treatment of DW in a CW treatment system. This treatment system resulted in 47% and 78% decrease in BOD and COD, respectively at incubation of 10 days. Increasing concentration of DW significantly reduced the biomass of growing plants, with the highest accumulation of Fe being recorded in plants growing in 100% concentration of DW. *Potamogeton pectinatus*, an aquatic macrophyte, was used to accumulate Mn, Zn, Cu, and Fe and efficiently clear out the DW (Singh et al. 2005). Chaturvedi et al. (2006) reported the phytoremediation potential of *P. australis* grown on DW-contaminated site. She also characterized the diverse bacterial species from the rhizospheric zone of *P. australis.* The culturable bacterial species were helpful for the degradation and decolorization of noxious pollutants that exist in the distillery effluent. They observed a 75.5% reduction of color by the same bacterial species along with a concomitant reduction in BOD, COD, sulfate, phenol, and HMs values. Bharagava et al. (2008) studied the HMs accumulation efficiency and its physiological effects in *Brassica nigra* L. (Indian mustard) plants grown in soil irrigated with different concentrations (25%, 50%, 75%, 100%, v/v) of PMDE after 30, 60, and 90 days treatment. This study concluded that *B. nigra* L. accumulated elevated concentrations of Zn, Ni, Mn, Fe, Cu, and Cd due to the increased amount of cysteine and ascorbic acid (work as antioxidants) in root, shoot, and leaves of *B. nigra* L. at all the concentrations and exposure periods of PMDE except at a 90-day period. Chandra and Yadav (2010) conducted a pot culture experiment to evaluate the accumulation pattern of Cu, Pb, Ni, Fe, Mn, and Zn in *T. angustifolia* grown in Zn, Mn, Fe, Ni, Pb, and Cu-rich aqueous solutions of phenols and melanoidins. They concluded that *T. angustifolia* could be an efficient phytoremediator for HMs from melanoidin, phenol, and metal-containing industrial effluent at optimized conditions. Recently, Hatano et al. (2016) observed the chelating property of melanoidin-like product (MLP) and to assess the facilitatory influence on the phytoextraction potential of *Raphanus sativus* var. *longipinnatus* (Japanese radish). They found that MLP binds with all the tested HMs ions, and the metal ion-binding capability of MLP toward Cu^{2+} was found to be the maximum among them. In a separate study Hatano and Yamatsu (2018) evaluated the facilitatory effect of MLP on phytoextraction potential of three *Brassica* species grown in a medium containing Pb or Cd. They reported that biomass and Pb^{2+} uptake in the nutrient medium containing 1 mM Pb nitrate were significantly increased by the addition of MLP, and all the Pb^{2+} from the medium was accumulated in the root tissues. They concluded that MLP was able to detoxify Pb^{2+} and to improve their bioavailability in *Brassica* species.

6.5.1.2.5 Vermifiltration

Vermifiltration technology is an alternative DW treatment method widely used in developing countries due to its low cost and eco-friendly nature. Manyuchi et al. (2018) reported that the TDS, TSS, TKN, BOD, and COD were significantly reduced by more than 90% during the 40 h vermifiltration process. The treated DW can be used for irrigation purposes. In addition, vermicompost, a bio-fertilizer which is rich in N (1.87%), P (0.66%), and K (0.87), was produced as part of the vermifiltration process.

6.5.1.2.6 Microbial Fuel Cells

Microbial fuel cells (MFCs), which exploit living microorganism as electrode catalysts, have the potential to recover energy from biomass wastes and distillery wastewater. It has recently attracted considerable attention as green energy devices for generating electricity from various organic and inorganic materials. Simultaneous electricity generation and DW treatment were accomplished using a thermophilic MFCs. Recently, molasses DW was examined as an organic fuel for electricity production in a mesophilic MFCs (Zhang et al. 2009; Mohanakrishna et al. 2009). Ha et al. (2012) studied the treatment of DW using a bacteroidetes-dominant thermophilic MFCs. The results suggest that thermophilic MFCs, which require less energy for cooling the DW, can achieve high efficiency for electricity generation and also reduce sulfate along with oxidizing complex organic substrates. Bacterial diversity analysis by pyrosequencing of the 16S rRNA gene showed that known *Deferribacteres* and *Firmicutes* members were not dominant in the thermophilic MFCs fed with DW; instead, uncharacterized *Bacteroidetes* thermophiles were up to 52% of the total reads in the anode biofilm. Recently, Mohamed et al. (2018) have investigated the effect of buffers and feed pH of the DW on the overall performance of the MFCs. The results demonstrated that anolyte of MFCs at pH 8 showed to achieved a maximum power density of 168 mW/m^2, which was due to the presence of microbial communities and its exoelectrogenic activity. In addition, the COD, TDS, and color elimination have achieved a maximum of 68.4%, 15.4%, and 26.4, respectively, at pH 8.

6.5.1.3 Emerging Treatment Approaches

6.5.1.3.1 Membrane Filtration

Membrane filtration (MF) is a term used to describe the removal of particulates from a feed stream (Chang et al. 1994). Tertiary treatment of aerobically treated DW by nanofiltration (NF) was carried out in a spiral wound NF membrane module, which was done by Rai et al. (2008) under different operating conditions. They obtained COD, TDS, and color removal in the range of 96–99.5%, 85–95%, 98–99.5%. respectively. The membrane-based NF and RO processes can be used to reduce the K$^+$ COD, TDS, and the content of DW by 99.99%, 99.90, and 99.80, respectively (Nataraj et al. 2006). Nakhla et al. (2006) studied the applicability of a submerged vacuum ultrafiltration membrane technology in combination with the biological treatment system. This system achieved 99% COD and 95–96.5% BOD removal. Submerged NF for removal of melanoidins from the BMDE was evaluated by Liu et al. (2013). The melanoidins could be effectively removed from the BMDE by SNF. However, MF technology cannot be directly applied to treat DW due to its high TDS.

6.5.1.3.2 Oxidation Processes

Oxidation processes are a set of chemical treatment procedures designed to remove organic (and sometimes inorganic) pollutants in DW by the formation of highly reactive oxidant species, mainly hydroxyl radicals (•OH), a powerful, ubiquitous in nature, nonselective, electrophilic behavior, redox potential of 2.8 V, and highly effective oxidants which accelerating the oxidation and destruction of a wide range of contaminants from wastewater by abstracting hydrogen atom from aliphatic carbon, or adding hydrogen atom to the double bonds and aromatic rings.

6.5.1.3.2.1 Ozone Oxidation

Ozone oxidation, also known as ozonation, is a promising technology for the treatment of DW. Ozone is a potent oxidant for wastewater treatment; when ozone comes in contact with wastewater, it reacts with organic compounds in two different ways: (i) direct oxidation as molecular ozone and (ii) indirect reaction through the formation of secondary oxidants like free radical species, viz., the •OH radicals. Both ozone and •OH radicals are strong oxidants and are capable of oxidizing a number of compounds, and, finally, COD value is reduced (Pena et al. 2003). The color elimination from DW was most likely due to the fact that ozone is able to break down the conjugated –C=C- bonds, thus breaking the chromophore of the melanoidins (Kim et al. 1985). Oxidation by ozone could achieve 80% decolorization of PMDE with simultaneous 15–25% COD reduction (Pena et al. 2003). Benitez et al. (2003) reported the reduction of COD and total aromatic compound up to 5–25.2% and 16.8–51.4% under optimum conditions by an ozonation process. A catalyst has also enhanced the efficiency of the ozonation process. Sangave et al. (2007) have used an ultrasound (US) plus ozone treatment process to treat DW pretreated with thermal pretreatment and AD process. The result demonstrated that 13% COD reduction was attained at the end of 48 h of aerobic oxidation, while 45.6% COD reduction was obtained in ozone-treated DW. Asaithambi et al. (2012) used a hybrid technique of ozone-assisted electrocoagulation for the elimination of COD and color in the industrial effluent. They reported a maximum elimination of COD (83%) at a current density of 3 Adm^{-2}, initial pH (6.0), and initial COD concentration 2500 ppm, and the ozone mixture flow rate was 15 L min^{-1}, while the complete elimination of color was found within 2 h of process time. Kumar et al. (2006) have reported that COD was removed up to 95% from treated PMDE through ozone treatment. Sreethawong and Chavadej (2008) have used iron oxide to enhance the ozone oxidation process. They reported a maximum 80% COD and 50% color reduction during the process.

6.5.1.3.2.2 Hydrogen Peroxide Treatment

The chemical decolorization of model melanoidins by H_2O_2 treatment was studied by Hayase et al. (1984). They reported about 64% and 97% decolorization of melanoidin using H_2O_2 at pH 7.0 and pH 10.0, respectively. They suggested the degradation of melanoidins by active oxygen species, i.e., H_2O_2, which is generated by the oxidation of glucose ($C_6H_{12}O_6$) into gluconic acid by the glucose-oxidase enzyme. They demonstrated that H_2O_2 reacts with hydroxyl anion (OH^-) to give per hydroxyl anion (HOO-), which nucleophilically attacks carbonyl groups (COOH) of melanoidins.

6.5.1.3.3 Photocatalytic Treatment

Photocatalytic degradation is an attractive treatment process for wastewater. Charles et al. (2015) studied the degradation of OM in the form of the color of SW using nano-photocatalyst nano-Al_2O_3/kaolin prepared from aluminum oxide (Al_2O_3) nanoparticle and kaolin clay. Optimization of the process parameters using Taguchi Orthogonal Array (TOA) design resulted in a maximum of 80% SW decolorization. A vanadium-doped TiO_2 (V-TiO_2) photocatalyst has been used for the degradation of SW and industrial dyes (Takle et al. 2018). The degradation of colored compounds in the SW was monitored by gel permeation chromatography, which showed the degradation of high molecular weight compounds into low molecular weight fractions.

6.5.2 Physicochemical Treatment Approaches

Physicochemical treatment methods are a combination of physical and chemical technologies used for wastewater treatment by adding chemicals. Elimination of suspended solids from the DW is a physical operation, while reduction of the dissolved solid is a chemical process. Several physicochemical methods, viz., coagulation/flocculation, electrocoagulation, thermolysis, membrane filtration, oxidation by ozone, chlorine dioxide, hydrogen peroxide, and radiation, and adsorption to material such as chitosan and activated carbon, have been shown to reduce the pollutant load of DW.

6.5.2.1 Adsorption

Activated carbon (AC) is the most extensively studied adsorbent prepared from agro-waste materials such as rice husk ash, fly ash, sugarcane bagasse, wood ash, and wood sawdust. This adsorbent has been reported to adsorb a wide array of organic compounds, i.e., phenolics, heavy metals, and other various organic pollutants and bio-organisms. Therefore, the adsorbent is used for the elimination of organic and inorganic pollutants in form color, COD, BOD, and HMs from DW (Chandra and Pandey 2000; Satyawali and Balakrishnan 2007, 2009; Mane et al. 2009). Comparative studies of color removal from DW using bagasse fly ash and commercial AC showed 58% color removal with 30 g/dm^3 of bagasse fly ash and 80.70% color removal with 20 g/dm^3 of commercial ACs. Lalov et al. (2000)

reported 98% color and 99% COD removal from DW by using natural carbohydrate polymer chitosan as an anion exchanger at 30 min contact time. ACs are not low-cost materials; hence, in spite of their good efficiency and applicability for adsorbing a wide variety of materials, their use can sometimes be restricted due to economic considerations.

6.5.2.2 Coagulation/Flocculation

Coagulation is the use of chemicals to cause pollutants to agglomerate and subsequently settle out during sedimentation. The removal of COD and color-containing compounds from DW was reported using inorganic coagulants, viz., aluminum chloride ($AlCl_3$), $FeCl_3$ (ferric chloride), calcium oxide (CaO), ferrous sulfate ($FeSO_4$), and polyaluminium chloride (PAC) (Chaudhari et al. 2007). Treatment of DW using iron sulfate [$Fe_2(SO_4)_3$] as a coagulant results in 40% removal of pollutants (Pikaev et al. 2001). Migo et al. (1993) studied the use of commercial inorganic flocculent $[Fe(OH)n(SO_4)3_{-n/2}]m$, a polymer of ferric hydroxide, for melanoidin removal from DW. Decolorization yields of 94%, 87%, and 32% were obtained for the lagoon, biodigester, and fresh slops effluents, respectively, at a flocculant dosage of 4% v/v. In addition, the reduction of TOC was 21% for fresh slops effluent and averaged to more than 73% for the biodigester and lagoon effluents. A 55% reduction in COD by using integrated Fenton-coagulant/flocculation process in distillery wastewater treatment has been reported by Beltrain de Heredia et al. (2005). *Moringa oleifera* seeds were also used as a coagulant for removal of color from SW (Krishna Prasad 2009). Armini et al. (2015) used manganese oxides, a strong oxidizer that oxidize aromatic amine to quinones and dimer products, for the color removal from melanoidin-rich DW. It can also oxidize the long-chain amines to nitrone, which may further dimerize to bigger compounds and precipitate out of the solution by MnOx. Different coagulants used by various researchers for the COD and decolorization of DW are shown in Table 6.6.

6.5.2.3 Electrochemical/Electrocoagulation

The electrochemical treatment methods (i.e., electrocoagulation) use electron as the main reagent as well as the presence of supporting electrolytes, to eliminate the OM from DW (Prasad and Srivastava 2009). This process involves the consumption of metals from the anode, with simultaneous formation of OH^- and H_2 occurring at the cathode. In the electrochemical treatment process, the pollutants are eliminated by either direct or indirect oxidation process (Kobya and Gengec 2012). In a direct oxidation process, the pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron transfer reaction, while, in an indirect oxidation process, strong oxidants, viz., hypochlorite (ClO^-)/chlorine (Cl), O_3, and H_2O_2 are electrochemically generated, and these oxidants destroyed the pollutants. Among the oxidants, ClO^- is cheaper, and DW has a certain amount of chloride (Cl^-). The electrochemical method converts Cl^- to ClO^-/Cl, through the supply of electrical current. The Cl and ClO^- oxidize the pollutants and are then reduced to chloride ions. Thakur et al. (2009) studied the effect of pH 3.5–9.0 on the electrochemical

Table 6.6 Reduction of COD and color from distillery wastewater investigated by different researchers by using a different coagulant

				Coagulant Performance		
S.No.	Feedstock	Type of distillery wastewater	Coagulant	COD reduction (%)	Color reduction (%)	References
1.	Molasses	–	$FeCl_3.6H_2O$	89.00	98.00	Liang et al. (2009a)
2.	Molasses	ATW	Aluminum sulfate	66.00	86.00	Liang et al. (2009b)
3.	Molasses	–	ACH/ polyDAMAC	56 0.00	70.00	Fan et al. (2011)
4.	Molasses	AADW	$FeCl_3.6H_2O$	90.00	90.00	Liakos and Lazaridis (2014)
5.	Molasses	ATW	$FeCl_3.6H_2O$	86.00	96.00	Liang et al. (2009)
6.	Sugar beet molasses	ATW	CaO	89.50	84.30	Inanc et al. (1999)
7.	Rice grain	–	$FeCl_3.6H_2O$	78.00	80.00	Prajapati et al. (2015)
8.	Cassava	ATW	$FeCl_3.6H_2O$	78.80	94.00	Zhang et al. (2017)

ATW anaerobically treated wastewater, *AADW* anaerobically digested wastewater, *DOM* dissolved organic matter, *COD* chemical oxygen demand

treatment of PMDE. The 31.5%, 43.71%, and 48.9% COD decline was obtained at pH 9.0, 6.5, and 3.5, respectively, with a current density of 117 A/m^2 in 60 min. Similarly, the effect of pH on the treatment of BMDE was studied by Kumar et al. (2009). The 32.66%, 39.95%, and 44% COD reduction was obtained at pH 2.0, 5.0, and 8.0, respectively, with a current density of 133.94 A/m^2 in 90 min. Prajapati and Chaudhari (2014) reported 87% color reduction and 93% COD reduction in DW using iron electrode at optimum condition.

6.5.2.4 Thermolysis

The treatment of DW by thermolysis is done due to the existence of a diverse range of compounds such as minerals, lignin, hemicellulose, proteins, lipids, and reduced carbohydrates in DW (Chaudhari et al. 2008). Lele et al. (1989) have studied the thermolysis process for treatment of SW at temperatures in the range of 160–250 °C and autogenous pressures. They observed that there was no further COD reduction after a treatment time of 2 h. The authors reported zero-order COD reduction kinetics as 6.67, 10.40, 10.8, and 14.40 kg/m^3 h at 160, 200, 230, and 250 °C, respectively. The thermolysis treatment of PMDE in the absence of air at 150 °F resulting in 35% COD reduction in t = 0.6 h has also been reported by Dhale and Mahajani (2000). Chaudhari et al. (2005) reported COD reduction of PMDE at 100 °C and atmospheric pressure by using different catalysts such as Mn/Cu oxide, Mn/Ce oxide, $CuSO_4$, and CuO. About 70%, 65%, 35%, 38%, 40%, and 36% COD reduction was obtained at pH 2.0, 2.0, 4.0, 6.0, 8.0, and 10, respectively, using CuO catalyst. Similarly, the treatment of SW with COD reduction of 58%, 60%, 51%, 36%, 30%, and 32% at pH 1, 2, 4, 6, 8, and 10, respectively at 140 °C and autogenous pressure was reported by Chaudhari et al. (2008).

6.6 Combined Biological Treatment Approaches

Since the SW contains recalcitrant highly colored pigments which cannot be separated or degraded with conventional treatment methods, there is always a lookout for advanced treatment methods. Besides, the drawbacks associated with these methods are instable decolorization efficiency, excess use of chemicals, operational difficulty, sensitivity to variable water input, and a huge amount of sludge generation with subsequent disposal problems, and occasional formation of hazardous by-products/secondary pollutants. Therefore, there are still demands to develop substitute means of decolorization and bioremediation of DW such as pioneering eco-friendly methods capable of providing a more complete cleanup of the pollutant in a more economic fashion. Investigation in implementing a hybrid method of treating the DW has gained its soundness rather than an individual treatment. In order to increase the biodegradation ability of the process, a two-stage sequential/phase separation/sequential method has demonstrated to be an efficient approach for bioremediation of DW. Numerous scientific reports indicated that the use of a hybrid technique by using bacteria, fungi, yeast, and plant or their combinatorial systems is more successful than the individual one. For instance, Ghosh et al. (2002) investigate the treatment of DW in a two-stage bioreactor by using *Pseudomonas putida* followed by *Aeromonas* sp. strain EMa. In the first stage, *P. putida* decreased the color and COD of DW up to 60% and 44.4, respectively, whereas in the second stage, *Aeromonas* sp. strain Ema reduced the effluent COD up to about 44.4%. Kaushik et al. (2010) investigated the treatment of DW in three-stage bioreactors by using fungus followed by bacteria. The potential use of fungi (*Cladosporium cladosporioides*) and cyanobacteria (*Phormidium valdernium*) for treatment of DW in a two-stage sequential step was also reported by Ravikumar and Kartik (2015). A maximum 68.5% decolorization and 81.37% COD reduction were achieved in the first-stage bioreactor during the batch experiment. Further, the SW from bioreactor was treated with cyanobacteria in the second stage and resulted in COD reduction (3652 mg L^{-1}) of 89.5% and 92.7% decolorization, respectively. Authors recommended that sequential treatment using the combination of fungi and cyanobacteria resulted in better decolorization and degradation of SW. Combination of wetland treatment technology after bacterial degradation offers an excellent system for the elimination of color from DW and reduction of BOD, COD, TDS, and HMs for safe disposal. A two-stage sequential treatment for sugarcane molasses-based PMDE was reported by Pant and Adholeya (2009a). In the first step, DW was treated in a hydroponic-based system using two plant species (*Vetiveria zizanioides* and *Phragmites karka*) to decrease the high nitrogen content up to 84% of the wastewater. The roots of these growing plants showed profuse growth on effluent. After that, this first stage treated DW was subjected for treatment by fungal isolates; 86.33% decolorization was obtained with *Pleurotus florida* Eger EM1303 followed by *Aspergillus flavus* TERIDB9 (74.67%), with a significant reduction in COD as well. Table 6.7 summarizes the two-stage sequential results of DW decolorization by using different organisms.

6.7 Reuse and Recycling of Distillery Effluent

In India, three popular methods are employed by distilleries to handle their wastewaters:

(i) Collection of DW in storage tanks, followed by irrigation.
(ii) DW treatment in settling lagoons, which are placed after AD, is found to be useful to settle the solids by gravity, evaporation processes, and application of resultant sludge on land. The outcome of evaporation is the formation of concentrated sludge that can be used as biofertilizer. Besides, distillery sludge is further incinerated to generate power, and the potassium-rich ash is recovered from the combustion of sludge.
(iii) The concentrated DW is used to make powders to use as raw material for power generation and mixed compound fertilizer. The overflow from settling lagoons is sent to RO plant where the permeate (water) of RO is recycled to the ethanol production unit, reducing the water requirement in distilleries. The reject of the RO plant is mixed with the press mud and marketed as a biocompost or discharge of the effluent to a local municipal treatment facility.

However, these three methods have their associated drawback and environmental risks. Tretament of lagoons through solar evaporation requires a huge ground region and also needs to take into consideration the weather conditions prevailing in the region, because settling lagoons are also non-functional during the monsoon. Moreover, treatment of DW in lagoons generates greenhouse gas emissions, and for irrigation practices may in some cases negatively affect the structure of aquifers, soils as well as groundwater quality.

6.7.1 Composting

Composting is a sustainable approach for bioconversion of organic residue of DW into compost (manure) through microorganisms (i.e., bacteria, actinomycetes, and fungi), and this manure may be utilized as nutrients for plant growth and development in the agricultural field. This approach not only solves the pollution and disposal problems arising from the DW and adopted by several Indian distilleries associated with sugar mills but also helps in saving the cost on chemical fertilizers (Bhalerao et al. 2006; Jadhav et al. 1992). Composting of DW is carried out using

Table 6.7 Treatment of distillery wastewater in two-stage sequential treatment by using different organisms

Effluent	First stage	Second stage	BOD	COD	Color	Dec	Incb	Reference
PMDE	Bacterial consortium	*Phragmites communis*	94.5%	96.0%	–	86.33%	–	Chandra et al. (2012)
BMSW	*Vetiveria zizanioides* and *Phragmites karka*)	*Pleurotus florida* and *Aspergillus flavus*	–	–	–	–	–	Pant and Adholeya (2009a)
PMDE	*Bacillus thuringiensis*	*Spirodela polyrrhiza* Schliden	–	–	–	–	–	Kumar and Chandra (2004)
PMDE	*Bacillus thuringiensis*	*Typha angustata* L.	98.00%	99.00%	–	–	7 days	Chandra et al. (2008)
SW	*Emiricella nidulans* var. lata. And *Neurospora intermedia*	*Bacillus* sp.	–	93.00%	82.00%	–	30 hrs	Kaushik et al. (2010)

PMDE post-methanated distillery effluent, *SW* spent wash, *BOD* biological oxygen demand, *COD* chemical oxygen demand, *BMSW* biomethanated spent wash, *hrs* hours, *Dec* decolourisation, *Incb* incubation period pressmud, obtained from sugarcane juice before the crystallization of sugar in sugar mills. It is the best source material for microbial growth and contains dark brown-colored, amorphous, lightweight, spongy material with 74%–75% OM, 20% volatile solids, 71% moisture, and 9% ash. In composting, DW either directly or after AD is sprayed on pressmud and mixed thoroughly using an aerotiller, which makes the pressmud aerable and enhances the decomposition process. The composting process of pressmud using PMDE wash has two unique features distinguishing it from other composting processes. One is the specially developed mixed microbial culture of fungi, bacteria, and actinomycetes, selected for their ability to rapidly degrade DW. The second is the conventional blending and mixing of the refuse comprising pressmud and liquid SW using the aerotiller machine. The integrated effect of farm yard manure (FYM), bio-compost, and BMDE as a source of plant nutrients and their effect on sugarcane yield, juice quality, nutrient uptake, and soil properties were investigated by Sinha et al. (2014). The quality of juice, viz., sucrose and purity, remains unaffected. The application of BMDE and bio-compost brings remarkable changes in the properties of soil and thus enhances the fertility of soil and productivity of sugarcane significantly.

6.7.2 Ferti-Irrigation

In India, most of the distillery units have opted DW for ferti-irrigation to improve soil health and crop productivity and alleviate environmental pollution problems. Some farmers in northern and western India living in the areas adjoining distilleries often use SW and SW-containing products as a source of manure without considering its impact on the soil and groundwater quality. However, DW also contains significant amounts of phosphorus (P), nitrogen (N), sulfur (S), and potassium (K^+), as well as easily biodegradable OM and micro- and macronutrients, viz., Zn, Cu, K, N, and Fe, which are essential for plant growth (Devarajan et al. 1994; Zalawadia and Raman 1994; Pathak et al. 1999; Yadav et al. 2010). Its application to soil at low concentration has been reported to be beneficial to increase mustard yield (Malaviya and Sharma 2011), wheat and rice (Pathak et al. 1998), rice (Deverajan and Oblisami 1995), sugar cane yield (Mohamed Haron and Subash Chandra Bose 2004), and physiological response of soybean and groundnut quality (Ramana et al. 2001). The use of DW in agriculture as a supplement for irrigation or soil amendment water in a judicious way to enhanced crop production as well as biological, chemical and physical properties of soil (Joshi et al. 1996; Jadhav and Savant 1975; Narain et al. 2012; Raverkar et al. 2000; Chidankumar et al. 2009; Ramana et al. 2001; Jain and Srivastava (2012). Singh et al. (1980) found that addition of SW without dilution was very effective in increasing water intake rate of the sodic calcareous soil. Zalawadia and Raman (1994) found that the application of DW in soil improved its water-retention characteristics. Ayyasamy et al. (2008) conducted a pot experiment to study the effects of different concentrations of sugar factory effluent on seed germination, seedling growth, and biochemical characteristics of green gram and maize. The higher effluent concentrations (above 60%) were found to affect plant growth, but diluted effluent (up to 60%) favored seedling growth. Previous studies revealed that the application of untreated DW to mung beans (*Vigna radiata*) and rice (*Oryza sativa* L.) suppressed seed germination and seedling growth, suggesting that pretreatment of the effluent to degrade OM before application to crops might yield better results (Arora et al. 1992; Kannan and Upreti 2008). Distillery application increased the dry matter yield and N recovery of Italian ryegrass compared to the inorganic NH_4-NO_3 fertilizer treatment (Douglas et al. 2003). Asano et al. (2014) reported that a large quantity of ammonium nitrogen (NH_4^+-N) was increased in rice-derived DW after inoculation with *A. caelatus*, *A. oryzae*, *A. tamarii*, and *B. subtilis* strain. Chauhan and Rai (2010) also indicated that irrigation with DW impaired the groundwater quality of Gajraula region, especially of agricultural zone, making it unsuitable for drinking purpose. Kumari et al. (2016) conducted field studies on *Brassica compestris* to assess the potential of the diluted PMDE. The results indicated that there was not much variation in pH, electrical conductivity, and nitrate of soil, whereas TDS, COD, and nitrate conductivity of the well water increased slightly but well within the permissible limit. However, there was a significant enhancement in the root hairs, the area of the leaf, diameter of the root and shoot, plant biomass, as well as number and length of pods. The application of BMDE @150 m^3 ha^{-1} can reduce fertilizer requirement, especially N by 75%, K_2O by 100%, and P_2O_5 by 20% (More et al. 2008). In ferti-irrigation, the yield of *Tritium aestivum* increased by 33% (Kumari et al. 2009) as compared to the control using diammonium phosphate and urea suggesting that the diluted DW is capable of replacing the application of chemical fertilizer when used under controlled conditions without any adverse effect on the soil and groundwater quality (Kumari et al. 2012). The use of DW as a soil amendment has generated interest in recent times. Most crops give higher yields with wastewater irrigation and decrease the need for chemical fertilizers, resulting in net cost savings to farmers. So it is an important aspect to understand the specificity of crop-effluent relationship for their appropriate application in irrigation practices. Kumar and Chopra (2012) have studied the ferti-irrigation effect of different concentrations of DW (5%, 10%, 25%, 50%, 75%, and 100%) on agronomical practices of *Trigonella foenum-graecum* L. (Fenugreek) along with control (bore well water). It was observed that there was a significant outcome on moisture content, PO_3^{-4}, SO_2^{-4}, NO_2^{-3}, TKN, Fe^{2+}, Mg^{2+}, Ca^{2+}, K^+, Na^+, CO^{-2}, HCO^{-3}, TOC, Cl^-, pH, and EC, and insignificant effect on WHC and bulk density after irrigation of soil with different DW concentrations up to 90 days. The agronomical parameters such as crop yield, LAI, chlorophyll content, dry weight, pods, flowers, number of leaves, root length, and shoot length of *T. foenum-graecum* were recorded to be in increasing order at low concentration of the DW, i.e., from 5% to 50%, and in decreasing order at higher DW concentration, i.e., from 75% to 100% as compared to control. The authors concluded that the long-term use of PMDE in agricultural fields may pose a serious threat to the groundwater quality.

6.8 Conclusion

The disposal of untreated or partially treated DW into the environment results in soil and water pollution leading to adverse effects on aquatic life and local vegetation. Thus, there is an urgent need to look into economically viable and easy-to-use technology for DW treatment. Several inexpensive secondary and tertiary treatment technologies including physicochemical and biological methods have been investigated for potential treatment of DW. However, these technologies are not techno-economic feasible options for mitigating the problems associated with the treatment and disposal of DW due to its complex nature of pollutants, which cannot be easily degraded by single-step treatment processes. Therefore, adequate treatment of DW by a novel two-step treatment/phase separation/sequential method by using organisms and their combinatorial systems has proven to be an effective approach for bioremediation of DW. The efficacy of the two-step treatment approach has been demonstrated under the pilot scale. This approach was found to be effective also in the field scale, and it is likely that during the next 5–10 years, its use will become widespread.

References

Acharya BK, Mohana S, Madamwar D (2008) Anaerobic treatment of distillery spent wash: a study on upflow anaerobic fixed film bioreactor. Bioresour Technol 99:4621–4626

Acharya BK, Pathak H, Mohana S, Shouche Y, Singh V, Madamwar D (2011) Kinetic modeling and microbial community assessment of anaerobic biphasic fixed film bioreactor treating distillery spent wash. Water Res 45:4248–4259

Adikane HV, Patale MB (2014) Biodegradation studies of non-sterile anaerobically treated distillery spent wash using *Aspergillus nidulans* isolated from irrigation site. Curr Biotechnol 3(2):174–179

Akunna JC, Clark M (2000) Performance of a granular-bed anaerobic baffled reactor (GRABBR) treating whisky distillery wastewater. Bioresour Technol 74(3):257–261

Alkorta I, Hernández-Allica J, Becerril JM, Amezaga I, Albizu I, Garbisu C (2004) Recent findings on the phytoremediation of soils contaminated with environmentally toxic heavy metals and metalloids such as Zinc, Cadmium, Lead, and Arsenic. Rev Environ Sci Biotechnol 3(1):71–90

Angayarkanni J, Palaniswamy M, Swaminathan K (2003) Biotreatment of distillery effluent using *Aspergillus niveus*. Bull Environ Contam Toxicol 70(2):268–277

Aoshima I, Tozawa Y, Ohmomo S, Ueda K (1985) Production of decolorizing activity for molasses pigment by Coriolus versicolor Ps4a. Agric Biol Chem 49:2041–2045

Arimi MM, Zhang Y, Goetz G, Kiriamiti K, Geissen SU (2014) Antimicrobial colorants in molasses distillery wastewater and their removal technologies. Int Biodeterior Biodegr 87:34–43

Arimi MM, Zhang Y, Götz G, Geisen S-U (2015) Treatment of melanoidin wastewater by anaerobic digestion and coagulation. Environ Technol 36(19):2410–2418

Arora M, Sharma D, Behera B (1992) Upgrading of distillery effluent by *Nitrosococcus oceanus* for its use as a low-cost fertilizer. Resour Conserv Recycl 6:347–353

Asaithambi P, Susree M, Saravanathamizhan R, Matheswaran M (2012) Ozone assisted electrocoagulation for the treatment of distillery effluent. Desalination 297:1–7

Asano R, Kobayashi S, Sonobe K, Shime-Hattori A, Okazaki K, Ohtomo R (2014) Plant-available inorganic nutrient levels are increased in rice-derived distillery effluents inoculated with microbes. J Appl Microbiol 117:1412–1421

Ayyasamy PM, Yasodha R, Rajakumar S, Lakshmanaperumalsamy P, Rahman PKSM, Lee S (2008) Impact of sugar factory effluent on the growth and biochemical characteristics of terrestrial and aquatic plants. Bull Environ Contam Toxicol 81:449–454

Beltrain de Heredia J, Domingues JR, Partido E (2005) Physico-chemical treatment for depuration of wine distillery wastewater (vinasses). Water Sci Technol 51(1):159–166

Benitez FJ, Real FJ, Acero JL, Garcia J, Sanchez M (2003) Kinetics of the ozonation and aerobic biodegradation of wine vinasses in discontinuous and continuous processes. J Hazard Mater B 101:203–218

Bhalerao VP, Jadhav MB, Bhoi PG (2006) Effect of spent wash, press mud and compost on soil properties, yield and quality of sugarcane. Indian Sugar 40(6):57–65

Bharagava RN, Chandra R (2010) Effect of bacteria treated and untreated post-methanated distillery effluent (PMDE) on seed germination, seedling growth and amylase activity in *Phaseolus mungo* L. J Hazard Mater 180:730–734

Bharagava RN, Chandra R, Rai V (2008) Phytoextraction of trace elements and physiological changes in Indian mustard plants (*Brassica nigra* L.) grown in post methanated distillery effluent (PMDE) irrigated soil. Bioresour Technol 99:8316–8324

Bharagava RN, Chandra R, Rai V (2009) Isolation and characterization of aerobic bacteria capable of the degradation of synthetic and natural melanoidins from distillery effluent. World J Microbiol Biotechnol 25(5):737–744

Billore SK, Singh N, Ram HK, Sharma JK, Singh VP, Nelson RM, Dass P (2001) Treatment of a molasses based distillery effluent in a constructed wetland in Central India. Water Sci Technol 44:441–448

Blonskaja V, Menert A, Vilu R (2003) Use of two-stage anaerobic treatment for distillery waste. Adv Environ Res 7:671–678

Bonugli-Santos RC, Durrant LR, Sette LD (2012) The production of ligninolytic enzymes by marine-derived basidiomycetes and their biotechnological potential in the biodegradation of recalcitrant pollutants and the treatment of textile effluents. Water Air Soil Pollut 223(5):2333–2345

Bories A, Raynal J, Bazile F (1988) Anaerobic digestion of high-strength distillery wastewater (cane molasses stillage) in a fixed-film reactor. Biol Wastes 23(4):251–267

Borja R, Martin A, Maestro R, Luque M, Durán J (1993) Enhancement of the anaerobic digestion of wine distillery wastewater by the removal of phenolic inhibitors. Bioresour Technol 45:99–104

Chandra R, Kumar V (2015a) Biotransformation and biodegradation of organophosphates and organohalides. In: Chandra R (ed) Environmental Waste Management. CRC Press, Boca Raton, pp 475–524. https://doi.org/10.1201/b19243-17.

Chandra R, Kumar V (2015b) Mechanism of wetland plant rhizosphere bacteria for bioremediation of pollutants in an aquatic ecosystem. In: Chandra R (ed) Advances in biodegradation and bioremediation of industrial waste. CRC Press, Boca Raton

Chandra R, Kumar V (2017a) Detection of androgenic-mutagenic compounds and potential autochthonous bacterial communities during in situ bioremediation of post methanated distillery sludge. Front Microbiol 8:887

Chandra R, Kumar V (2017b) Detection of *Bacillus* and *Stenotrophomonas* species growing in an organic acid and endocrine-disrupting chemicals rich environment of distillery spent wash and its phytotoxicity. Environ Monit Assess 189:26

Chandra R, Kumar V (2017c) Phytoextraction of heavy metals by potential native plants and their microscopic observation of root growing on stabilized distillery sludge as a prospective tool for in-situ phytoremediation of industrial waste. Environ Sci Pollut Res 24:2605–2619

Chandra R, Kumar V (2018) Phytoremediation: a green sustainable technology for industrial waste management. In: Chandra R, Dubey NK, Kumar V (eds) Phytoremediation of environmental pollutants. CRC Press, Boca Raton

Chandra R, Pandey PK (2000) Decolourization of anaerobically-treated distillery effluent by activated charcoal adsorption method. Indian J Environ Prot 21:134–137

Chandra R, Kumar V, Tripathi S (2018a) Evaluation of molasses-melanoidin decolorisation by potential bacterial consortium discharged in distillery effluent. 3 Biotech 8:187

Chandra R, Kumar V, Tripathi S, Sharma P (2018b) Heavy metal phytoextraction potential of native weeds and grasses from endocrine-disrupting chemicals rich complex distillery sludge and their histological observations during in situ phytoremediation. Ecol Eng 111:143–156

Chandra R, Kumar V, Tripathi S, Sharma P (2018c) Phytoremediation of industrial pollutants and life cycle assessment. In: Chandra R, Dubey NK, Kumar V (eds) Phytoremediation of environmental pollutants. CRC Press, Boca Raton

Chandra R, Kumar V, Singh K (2018d) Hyperaccumulator versus nonhyperaccumulator plants for environmental waste management. In: Chandra R, Dubey NK, Kumar V (eds) Phytoremediation of environmental pollutants. CRC Press, Boca Raton

Chandra R, Kumar V, Yadav S (2017) Extremophilic ligninolytic enzymes. In: Sani R, Krishnaraj R (eds) Extremophilic enzymatic processing of lignocellulosic feedstocks to bioenergy. Springer

Chandra R, Saxena G, Kumar V (2015) Phytoremediation of environmental pollutants: an eco-sustainable green technology to environmental management. In: Chandra R (ed) Advances in biodegradation and bioremediation of industrial waste. CRC Press, Boca Raton, pp 1–29

Chandra R, Bharagava RN, Kapley A, Purohit HJ (2012) Characterization of *Phragmites cummunis* rhizosphere bacterial communities and metabolic products during the two stage sequential treatment of post methanated distillery effluent by bacteria and wetland plants. Bioresour Technol 103:78–86

Chandra R, Yadav S, Bharagava RN, Murthy RC (2008) Bacterial pretreatment enhances removal of heavy metals during treatment of post-methanated distillery effluent by *Typha angustata* L. J Environ Manag 88:1016–1024

Chandraju S, Basavaraju HC (2007) Impact of distillery spent wash on seed germination and growth of leaves vegetables: an investigation. Sugar J (SISSTA) 38:20–50

Chandralata R, Mohandass C, Shilpa K, Shailaja MS (2004) Simultaneous detoxification and decolorization of molasses spent wash by the immobilized white-rot fungus *Flavodon flavus* isolated from a marine habitat. Enzym Microb Technol 35(2–3):197–202

Chang IS, Choo KH, Lee CH, Pek UH, Koh UC, Kim SW, Koh JH (1994) Application of ceramic membrane as a pre-treatment in anaerobic digestion of alcohol-distillery wastes. J Memb Sci 90(1–2):131–139

Charles D, Arivazhagan M, Balamurali MN, Shanmugarajan D (2015) Decolorization of distillery spent wash using biopolymer synthesized by isolated from tannery effluent. Biomed Res Int 2015:1–9

Chaturvedi S, Chandra R, Rai V (2006) Isolation and characterization of *Phragmites australis* (L.) rhizosphere bacteria from contaminated site for bioremediation of colored distillery effluent. Ecol Eng 27:202–207

Chaudhari PK, Mishra IM, Chand S (2005) Catalytic thermal treatment (catalytic thermolysis) of a biodigester effluent of an alcohol distillery plant. Ind Eng Chem Res 44(15):5518–5525

Chaudhari PK, Mishra IM, Chand S (2007) Decolourization and removal of chemical oxygen demand (COD) with energy recovery: treatment of biodigester effluent of a molasses-based alcohol distillery using inorganic coagulants. Colloids Surf A Physicochem Eng Asp 296(1–3):238–247

Chaudhari PK, Mishra IM, Chand S (2008) Effluent treatment of alcohol distillery: catalytic thermal pretreatment (catalytic thermolysis) with energy recovery. Chem Eng J 136:14–24

Chauhan J, Rai JPN (2010) Monitoring of impact of ferti-irrigation by postmethanated distillery effluent on groundwater quality. Clean Soil, Air, Water 38(7):630–638

Chavan MN, Dandi ND, Kulkarni MV, Chaudhari AB (2013) Biotreatment of melanoidin-containing distillery spent wash effluent by free and immobilized *Aspergillus oryzae* MTCC 7691. Water Air Soil Pollut 224(11):5

Chidankumar CS, Chandaraju S, Nagendra Swamy R (2009) Impact of distillery spent wash irrigation on the yields of some root vegetables in untreated and spent wash treated soil. SISSTA 40:233–236

Collins G, Foy C, McHugh S, Maho T, O'Flaherty V (2005) Anaerobic biological treatment of phenolic wastewater at 15–18°C. Water Res 39:1614–1620

Dahiya J, Sing D, Nigam P (2001) Decolourisation of synthetic and spent wash melanoidins using the white-rot fungus *Phanerochaete chrysosporium* JAG-40. Bioresour Technol 78:95–98

Davamani V, Lourduraj AC, Singaram P (2006) Effect of sugar and distillery wastes on nutrient status, yield and quality of turmeric. Crop Research Hisar 32(3):563–567

Devarajan L, Rajanan G, Ramanathan G, Oblisami G (1994) Performance of field crops under distillery effluent irrigations. Kisan World 21:48–50

Deverajan L, Oblisami G (1995) Effect of distillery effluent on soil fertility status, yield and quality of rice. Madras Agric J 82:664–665

Dhale AD, Mahajani VV (2000) Treatment of distillery waste water after bio-gas generation: wet oxidation. Indian J Chem Technol 7(1):11–18

Douglas JT, Aitken MN, Smith CA (2003) Effects of five non-agricultural organic wastes on soil composition, and on the yield and nitrogen recovery of Italian ryegrass. Soil Use Manag 19(2):15–138

D'Souza DT, Tiwari R, Sah AK, Raghukumar C (2006) Enhanced production of laccase by a marine fungus during treatment of colored effluents and synthetic dyes. Enzym Microb Technol 38(3-4):504–511

Fahy V, FitzGibbon FJ, McMullan G, Singh D, Marchant R (1997) Decolourisation of molasses spent wash by *Phanerochaete chrysosporium*. Biotechnol Lett 19(1):97–99

Fan L, Nguyen T, Roddick FA (2011) Characterisation of the impact of coagulation and anaerobic bio-treatment on the removal of chromophores from molasses wastewater. Water Res 45(13):3933–3940

Ghosh M, Ganguli A, Tripathi AK (2002) Treatment of anaerobically digested distillery spent wash by a two stage bioreactor using *Pseudomonas putida* and *Aeromonas* sp. Process Biochem 37(8):857–862

Ghosh M, Verma SC, Mengoni A, Tripathi AK (2004) Enrichment and identification of bacteria capable of reducing chemical oxygen demand of anaerobically treated molasses spent wash. J Appl Microbiol 96(6):1278–1286

Glick BR (2010) Using soil bacteria to facilitate phytoremediation. Biotechnol Adv 28(3):367–374

Gonzalez T, Terron MC, Yague S, Zapico E, Galletti GC, Gonzalez AE (2000) Pyrolysis/gas chromatography/mass spectrometry monitoring of fungal-biotreated distillery wastewater using *Trametes s*p. I-62 (CECT 20197). Rapid Commun Mass Spectrom 14(15):1417–1424

González T, Terrón MC, Yagüe S, Junca H, Carbajo JM, Zapico EJ, Silva R, Arana-Cuenca A, Téllez A, González AE (2008) Melanoidincontaining wastewaters induce selective laccase gene expression in the white-rot fungus *Trametes* sp. I-62. Res Microbiol 159(2):103–109

Ha PT, Lee TK, Rittmann BE, Park J, Chang IS (2012) Treatment of alcohol distillery wastewater using a bacteroidetes-dominant thermophilic microbial fuel cell. Environ Sci Technol 46:3022–3030

Harada H, Uemura S, Chen A-C, Jayadevan J (1996) Anaerobic treatment of a recalcitrant distillery wastewater by a thermophilic UASB reactor. Bioresour Technol 55(3):215–221

Hatano K, Komatsu I, Aoyagi N, Takahashi K, Kubota K (2013) A study on the self-assembly behavior of dark materials from molasses. Environ Sci Pollut Res 20:4009–4017

Hatano K-I, Kanazawa K, Tomura H, Yamatsu T, Tsunoda K-i, Kubota K (2016) Molasses melanoidin promotes copper uptake for radish sprouts: the potential for an accelerator of phytoextraction. Environ Sci Pollut Res 23(17):17656–17663

Hatano K, Yamatsu T (2018) Molasses melanoidin-like products enhance phytoextraction of lead through three Brassica species. Int J Phytoremediation. https://doi.org/10.1080/15226514.2017.1393397

Hayase F, Kim SB, Kato H (1984) Decolorization and degradation products of the melanoidins by hydrogen peroxide. Agric Biol Chem 48(11):2711–2717

Inanc B, Ciner F, Ozturk I (1999) Colour removal from fermentation industry effluents. Water Sci Technol 40(1):331–338

Jadhav HD, Savant NK (1975) Influence of added spent wash (distillery waste) on chemical and physical properties of soil. Indian J Agric Chem 8:78–84

Jadhav MB, Joshi VA, Jagtap PB, Jadhav SB (1992) Effect spent wash press mud cake compost on soil physicochemical. Biological properties, yield and quality of adsali sugarcane. Ann Convention DSTA II:119–134

Jagdale HN, Sawant NK (1975) Influence of added spent wash (Distillery waste) on growth and chemical composition of immature sugarcane (Saccharum officinarum L.) cultivar CO-740. Indian Sugar 29(7):433–440

Jain R, Srivastava S (2012) Nutrient composition of spent wash and its impact on sugarcane growth and biochemical attributes. Physiol Mol Biol Plants 18(1):95–99

Jiranuntipon S, Chareonpornwattana S, Damronglerd S, Albasi C, Delia M-L (2008) Decolorization of synthetic melanoidins-containing wastewater by a bacterial consortium. J Ind Microbiol Biotechnol 35(11):1313–1321

Jiranuntipon S, Delia M-L, Albasi C, Damronglerd S, Chareonpornwattana S (2009) Decolourization of molasses based distillery wastewater using a bacterial consortium. ScienceAsia 35(4):332

Joshi HC, Kalra N, Chaudhary A, Deb DL (1994) Environmental issues related with distillery effluent utilization in agriculture in India. Asia Pacific J Environ Dev 1:92–103

Joshi HC, Pathak H, Chaudary A, Kalra N (1996) Distillery effluent as a source of plant nutrients: prospects and problems. Fert News 41:41–47

Joshi HC, Pathak H, Chaudhary A, Joshi TP, Phogat VK, Kalra N (2000) Changes in soil properties with distillery effluent irrigation. J Environ Res 6(4):153–162

Kalavathi DF, Uma L, Subramanian G (2001) Degradation and metabolization of the pigment—melanoidin in distillery effluent by the marine cyanobacterium *Oscillatoria boryana* BDU 92181. Enzy Microb Technol 29:246–251

Kambe TN, Shimomura M, Nomura N, Chanpornpong T, Nakahara T (1999) Decolourization of molasses wastewater by *Bacillus* sp. under thermophilic and anaerobic conditions. J Biosci Bioeng 87:119–121

Kannan A, Upreti R (2008) Influence of distillery effluent on germination and growth of mung bean (*Vigna radiata*) seeds. J Hazard Mater 153:609–615

Kaushik G, Thakur IS (2009) Isolation of fungi and optimization of process parameters for decolorization of distillery mill effluent. World J Microbiol Biotechnol 25(6):955–964

Kaushik G, Thakur IS (2013) Adsorption of colored pollutants from distillery spent wash by native and treated fungus: *Neurospora intermedia*. Environ Sci Pollut Res 20(2):1070–1078

Kaushik G, Gopal M, Thakur IS (2010) Evaluation of performance and community dynamics of microorganisms during treatment of distillery spent wash in a three stage bioreactor. Bioresour Technol 101:4296–4305

Kaushik A, Nisha R, Jagjeeta K, Kaushik CP (2005) Impact of long and short term irrigation of a sodic soil with distillery effluent in combination with bioamendments. Bioresour Technol 96:1860–1866

Keyser M, Witthuhn RC, Ronquest LC, Britz TJ (2003) Treatment of winery effluent with upflow anaerobic sludge blanket (UASB)–granular sludges enriched with *Enterobacter sakazakii*. Biotechnol Lett 25(22):1893–1898

Kim SB, Hayase F, Kato H (1985) Decolourisation and degradation products of melanoidin on ozonolysis. Agric Biol Chem 49:785–792

Kim SJ, Shoda M (1999) Batch decolorization of molasses by suspended and immobilized fungus of *Geotrichum candidum*. J Biosci Bioeng 88(5):586–589

Kobya M, Gengec E (2012) Decolourization of melanoidins by a electrocoagulation process using aluminium electrodes. Environ Technol 33(21):2429–2438

Krishna Prasad R (2009) Color removal from distillery spent wash through coagulation using *Moringa oleifera* seeds: use of optimum response surface methodology. J Hazard Mater 165(1–3):804–811

Krishnamoorthy S, Premalatha M, Vijayasekaran M (2017) Characterization of distillery wastewater–an approach to retrofit existing effluent treatment plant operation with phycoremediation. J Clea Produc 148:735–750

Krzywonos M (2012) Decolorization of sugar beet distillery effluent using mixed cultures of bacteria of the genus Bacillus. Afr J Biotechnol 11(14):3464–3475

Krzywonos M, Seruga P (2012) Decolorization of sugar beet molasses vinasse, a high-strength distillery wastewater, by lactic acid bacteria. Pol J Environ Stud 21(4):943–948

Kumar P, Chandra R (2004) Detoxification of distillery effluent through *Bacillus thuringiensis* (MTCC 4714) enhanced phytoremediation potential of *Spirodela polyrrhiza* (L.) Schliden. Bull Environ Contam Toxicol 73:903–910

Kumar P, Chandra R (2006) Decolourisation and detoxification of synthetic molasses melanoidins by individual and mixed cultures of *Bacillus* spp. Bioresour Technol 97:2096–2102

Kumar V, Chandra R (2018) Characterisation of manganese peroxidase and laccase producing bacteria capable for degradation of sucrose glutamic acid-maillard products at different nutritional and environmental conditions. World J Microbiol Biotechnol 34:32

Kumar V, Chandra R (2020) Bioremediation of melanoidins containing distillery waste for environmental safety. In: Saxena G, Bharagava RN (eds) Bioremediation of Industrial Waste for Environmental Safety. Vol II- Microbes and Methods for Industrial Waste Management. Springer

Kumar V, Chopra AK (2012) Fertigation effect of distillery effluent on agronomical practices of *Trigonella foenum-graecum* L. (fenugreek). Environ Monit Assess 184(3):1207–1219

Kumar S, Gopal K (2001) Impact of distillery effluent on physiological consequences in the fresh water teleost *Channa punctatus*. Bull Environ Contam Toxicol 66:617–622

Kumar V, Sharma DC (2019) Distillery effluent: Pollution profile, eco-friendly treatment strategies, challenges, and future prospects. In: Arora PK (eds) Microbial metabolism of xenobiotic compounds. Springer Nature. https://doi.org/10.1007/978-981-13-7462-3_17

Kumar M, Infant F, Ponselvan A, Malviya JR, Srivastava VC, Mall ID (2009) Treatment of biodigester effluent by electrocoagulation using iron electrodes. J Hazard Mater 165:345–352

Kumar A, Saroj DP, Tare V, Bose P (2006) Treatment of distillery spent-wash by ozonation and biodegradation: Significance of pH reduction and inorganic carbon removal before ozonation. Water Environ Res 78(9):994–1004

Kumar V, Shahi SK, Singh S (2018) Bioremediation: an eco-sustainable approach for restoration of contaminated sites. In: Singh J, Sharma D, Kumar G, Sharma NR (eds) Microbial bioprospecting for sustainable development. Springer, Sharma

Kumar V, Wati L, Fitz Gibbon F, Nigan P, Banat IM, Singh D, Marchant R (1997) Bioremediation and decolorization of anaerobically digested distillery spent wash. Biotechnol Lett 19:311–313

Kumar V, Wati L, Nigam P, Banat IM, Yadav BS, Singh D, Marchant R (1998) Decolorization and biodegradation of anaerobically digested sugarcane molasses spent wash effluent from biomethanation plants bywhite-rot fungi. Process Biochem 33(1):83–88

Kumari K, Ranjan N, Ray SNC, Aggarwal PK, Sinha RC (2009) Eco-friendly utilization of diluted distillery effluent on the morphological, physiological and biochemical parameters in the wheat plant "*Triticum aestivum*". Int J Bioved 20:1–8

Kumari K, Ranjan N, Sharma JP, Aggarwal PK, Sinha RC (2012) Integrated management of diluted distillery effluent and fly ash as a potential biofertilizer: a case study on the vegetative growth and chlorophyll content of the marigold plant, "*Tagetespatula*". Int J Environ Tech Manag 15:275–290

Kumari K, Ranjan N, Kumar S, Sinha RC (2016) Distillery effluent as a liquid fertilizer: a win–win option for sustainable agriculture. Environ Technol 37(3):381–387

Lalov IG, Guerginov II, Krysteva A, Fartsov K (2000) Treatment of wastewater from distilleries with chitosan. Water Res 34(5):1503–1506

Lele SS, Rajadhyaksha PJ, Joshi JB (1989) Effluent treatment for alcohol distillery: thermal pretreatment with energy recovery. Environ Prog 8:245–252

Liakos TI, Lazaridis NK (2014) Melanoidins removal from simulated and real wastewaters by coagulation and electro-flotation. Chem Eng J 242:269–277

Liang Z, Wang Y, Yu Z, Liu H (2009a) Coagulation removal of melanoidins from biologically treated molasses wastewater using ferric chloride. Chem Eng J 152(1):88–94

Liang Z, Wang Y, Yu Z, Liu H, Wu Z (2009b) Variables affecting melanoidins removal from molasses wastewater by coagulation/flocculation. Sep Purif Technol 68(3):382–389

Liu J, Zhang X (2014) Comparative toxicity of new halophenolic DBPs in chlorinated saline wastewater effluents against a marine alga: halophenolic DBPs are generally more toxic than haloaliphatic ones. Water Res 65:64–72

Liu M, Zhu H, Dong B, Zheng Y, Yu S, Gao C (2013) Submerged nanofiltration of biologically treated molasses fermentation wastewater for the removal of melanoidins. Chem Eng J 223:388–394

López I, Borzacconi L, Passeggi M (2018) Anaerobic treatment of sugar cane vinasse: treatability and real-scale operation. J Chem Technol Biotechnol 93:1320–1327

Ma Y, Prasad MNV, Rajkumar M, Freitas H (2011) Plant growth promoting rhizobacteria and endophytes accelerate phytoremediation of metalliferous soils. Biotechnol Adv 29(2):248–258

Mahgoub S, Tsioptsias C, Samaras P (2016) Biodegradation and decolorization of melanoidin solutions by manganese peroxidase yeasts. Water Sci Technol 73(10):2436–2445

Malaviya P, Sharma A (2011) Effect of distillery effluent on yield attributes of *Brassica napus L.* J Environ Biol 32:385–389

Mane JD, Modi S, Nagawade S, Phadnis SP, Bhandari VM (2009) Treatment of Spentwash using chemically modified bagasse and color removal studies. Bioresour Technol 97:1752–1755

Manyuchi MM, Mbohwa C, Muzenda E (2018) Biological treatment of distillery wastewater by application of the vermifiltration technology. South Afr J Chem Eng 25:74–78

Mehta J, Yadav A, Dilbaghi N, Sharma P (2014) Physicochemical characterization of distillery effluent and COD reduction by using *Bacillus badius* and *Lysinibacillus fusiformis*. Int J Emerg Trends Sci Technol 1(3):340–346

Migo VP, Del Rosario EJ, Matsumura M (1997) Flocculation of melanoidins induced by inorganic ions. J Ferment Bioeng 83(3):287–291

Migo VP, Matsumura M, Delrosario EJ, Kataoka H (1993) Decolorization of molasses wastewater using an inorganic flocculent. J Ferment Bioeng:75–438

Miyata N, Iwahori K, Fujita M (1998) Manganese-independent and -dependent decolorization of melanoidin by extracellular hydrogen peroxide and peroxidases from *Coriolus hirsutus* pellets. J Ferment Bioeng 85(5):550–553

Miyata N, Mori T, Iwahori K, Fujita M (2000) Microbial decolorization of melanoidin-containing wastewaters: combined use of activated sludge and the fungus *Coriolus hirsutus*. J Biosci Bioeng 89(2):145–150

Moletta R (2005) Winery and distillery wastewater treatment by anaerobic digestion. Water Sci Technol 51(1):137–144

Mohammad P, Azarmidokht H, Fatollah M, Mahboubeh B (2006) Application of response surface methodology for optimization of important parameters in decolorizing treated distillery wastewater using *Aspergillus fumigatus* UB2 60. Int Biodeterior Biodegrad 57(4):195–199

Mohamed SN, Karunakaran RT, Manickam M (2018) Enhancement of bioelectricity generation from treatment of distillery wastewater using microbial fuel cell. Environ Progress Sustain Energy 37(2):663–668

Mohamed Haron AR, Subash Chandra Bose M (2004) Use of distillery spent wash for alkali soil reclamation, treated distillery effluent for ferti-irrigation of crops. Indian Farming 3:48–51

Mohana S, Desai C, Madamwar D (2007) Biodegradation and decolourization of anaerobically treated distillery spent wash by a novel bacterial consortium. Bioresour Technol 98(2):333–339

Mohanakrishna G, Venkata Mohan S, Sarma PN (2009) Bioelectrochemical treatment of distillery wastewater in microbial fuel cell facilitating decolorization and desalination along with power generation. J Hazard Mater 177(1–3):487-–494

More NB, Shinde NJ, Pol KM (2008) Utilization of distillery effluent in agriculture. Indian Sugar 58:31–61

Nakhla G, Lugowski A, Patel J, Rivest V (2006) Combined biological and membrane treatment method processing wastewater to achieve dry-ditch criteria: pilot and full scale performance. Bioresour Technol 99:1–14

Narain K, Yazdani T, Bhat MM, Yunus M (2012) Effect on physico-chemical and structural properties of soil amended with distillery effluent and ameliorated by cropping two cereal plant spp. Environ Earth Sci 66:977–984

Nataraj SK, Hosamani KM, Aminabhavi TM (2006) Distillery wastewater treatment by the membrane-based nanofiltration and reverse osmosis processes. Water Res 40(12):2349–2356

Pant D, Adholeya A (2007) Identification, ligninolytic enzyme activity and decolorization potential of two fungi isolated from a distillery effluent contaminated site. Water Air Soil Pollut 183(1–4):165–176

Pant D, Adholeya A (2009a) Nitrogen removal from biomethanated spent wash using hydroponic treatment followed by fungal decolorization. Environ Eng Sci 26:559–565

Pant D, Adholeya A (2009b) Concentration of fungal ligninolytic enzymes by ultrafiltration and their use in distillery effluent decolorization. World J Microbiol Biotechnol 25:1793–1800

Pathak H, Joshi HC, Chaudhary A, Karla N, Dwivedi MK (1998) Distillery effluent as soil amendment for wheat and rice. J Indian Soil Sci 46:155–157

Pathak H, Joshi HC, Chaudhary A, Chaudhary R, Kalra N, Dwiwedi MK (1999) Soil amendment with distillery effluent for wheat and rice cultivation. Water, Air, Soil Pollu 113:133–140

Pena M, Coca M, Gonzalez G, Rioja R, Garcia MT (2003) Chemical oxidation of wastewater from molasses fermentation with ozone. Chemosphere 51:893–900

Pikaev AK, Ponomarev AV, Bludenko AV, Minin VN, Elizar'eva LM (2001) Combined electronic-beam and coagulation purification of molasses distillery slops. Features of the method, technical and economic evaluation of large scale facility. Rad Phy Chem 61(1):81–87

Prajapati A, Chaudhari P (2014) Electrochemical treatment of rice grain based distillery effluent: chemical oxygen demand and color removal. Environ Technol 35:242–248

Prajapati AK, Choudhary R, Verma K, Chaudhari PK, Dubey A (2015) Decolorization and removal of chemical oxygen demand (COD) of rice grain–based biodigester distillery effluent (BDE) using inorganic coagulants. Desalin Water Treat 53(8):2204–2214

Prasad RK, Srivastava SN (2009) Electrochemical degradation of distillery spent wash using catalytic anode: factorial design of cexperiments. Chem Eng J 146:22–29

Rajkumar M, Freitas H (2008) Influence of metal resistant-plant growth-promoting bacteria on the growth of Ricinus communis in soil contaminated with heavy metals. Chemosphere 71(5):834–842

Raghukumar C, Rivonkar G (2001) Decolorization of molasses spent wash by the white-rot fungus Flavodon flavus, isolated from a marine habitat. Appl Microbiol Biotechnol 55(4):510–514

Rai UK, Muthukrishnan M, Guha BK (2008) Tertiary treatment of distillery wastewater by nanofiltration. Desalination 230(1–3):70–78

Ramakritinan CM, Kumaraguru AK, Balasubramanian MP (2005) Impact of distillery effluent on carbohydrate metabolism of freshwater fish, *Cyprinus carpio*. Ecotoxicology 14(7):693–707

Ramana S, Biswas AK, Kundu S, Saha JK, Yadava BR (2001) Effect of distillery effluent on seed germination in some vegetable crops. Bioresour Technol 82:273–275

Raverkar KP, Ramana S, Singh AB, Biswas AK, Kundu S (2000) Impact of post response of soyabean (*Glycine max* L.) to foliar application of distillery effluent. Ann Plant Soil Res 2:1–6

Ravikumar R, Karthik V (2015) Effective utilization and conversion of spent distillery liquid to valuable products using an intensified technology of two-stage biological sequestration. Chem Biochem Eng Q 29(4):599–608

Ravikumar R, Vasanthi NS, Saravanan K (2011) Single factorial experimental design for decolorizing anaerobically treated distillery spent wash using cladosporium cladosporioides. Int J Environ Sci Technol 8(1):97–106

Ravikumar R, Vasanthi NS, Saravanan K (2013) Biodegradation and decolorization of distillery spent wash with product release by a novel strain *Cladosporium cladosporioides:* optimization and Biokinetics. Chem Biochem Eng Q 27(3):373–383

Saini JK, Lohchab RK (2017) Performance of UASB reactor to treat distillery spent wash under various operating conditions. Ann Biol 33(1):10–15

Saner AB, Mungray AK, Mistry NJ (2014) Treatment of distillery wastewater in an upflow anaerobic sludge blanket (UASB) reactor. Desal WatTreat:1–17

Sangave PC, Gogate PR, Pandit AB (2007) Ultrasound and ozone assisted biological degradation of thermally pretreated and anaerobically pretreated distillery wastewater. Chemosphere 68:42–50

Sankaran K, Lakshmi P, Suriya Narayanan G, Premalatha M (2015) Bacterial assisted treatment of anaerobically digested distillery wastewater. RSC Adv 5(87):70977–70984

Santal AR, Singh NP, Saharan BS (2011) Biodegradation and detoxification of melanoidin from distillery effluent using an aerobic bacterial strain SAG of *Alcaligenes faecalis*. J Hazard Mater 193:319–324

Santal AR, Singh NP, Saharan BS (2016) A novel application of Paracoccus pantotrophus for the decolorization of melanoidins from distillery effluent under static conditions. J Environ Manag 169:78–83

Satyawali Y, Balakrishnan M (2007) Removal of color from biomethanated distillery spentwash by treatment with activated carbons. Bioresour Technol 98(14):2629–2653

Satyawali Y, Balakrishnan M (2009) Performance enhancement with powdered activated carbon (PAC) addition in a membrane bioreactor (MBR) treating distillery effluent. J Hazard Mater 170:457–465

Singh SS, Dikshit AK (2011) Decolourization of anaerobically digested and polyaluminium chloride treated distillery spentwash in a fungal stirred tank aerobic reactor. Biodegradation 22(6):1109–1117

Singh NK, Pandey GC, Rai UN, Tripathi RD, Singh HB, Gupta DK (2005) Metal accumulation and ecophysiological effects of distillery effluent on *Potamogeton pectinatus* L. Bull Environ Contam Toxicol 74:857–863

Singh R, Singh NT, Arora Y (1980) The use of spent wash for the reclamation of sodic soils. J Indian Soc Soil Sci 28:38–41

Sinha SK, Jha CK, Kumar V, Kumari G, Alam M (2014) Integrated effect of bio-methanated distillery effluent and bio-compost on soil properties, juice quality and yield of sugarcane in entisol. Sugar Tech 16(1):75–79

Sirianuntapiboon S, Zohsalam P, Ohmomo S (2004) Decolorization of molasses wastewater by Citeromyces sp. WR-43-6. Process Biochem 39(8):917–924

Solovchenko A, Pogosyan S, Chivkunova O, Selyakh I, Semenova L, Voronova E, Scherbakov P, Konyukhov I, Chekanov K, Kirpichnikov M, Lobakova E (2014) Phycoremediation of alcohol distillery wastewater with a novel *Chlorella sorokiniana* strain cultivated in a photobioreactor monitored on-line via chlorophyll fluorescence. Algal Res 6:234–241

Sreethawong T, Chavadej S (2008) Color removal of distillery wastewater by ozonation in the absence and presence of immobilized iron oxide catalyst. J Hazard Mater 155:486–493

Srivastava S, Jai R (2010) Effect of distillery spent wash on cytomorphological behaviour of sugarcane settlings. J Environ Res 31:809–812

Takle SP, Naik SD, Khore SK, Ohwal SA, Bhujbal NM, Landge SL, Kale BB, Sonawane RS (2018) Photodegradation of spent wash, a sugar industry waste, using vanadium-doped TiO nanoparticles. RSC Adv 8:20394

Tapia-Tussell R, Pérez-Brito D, Torres-Calzada C, Cortés-Velázquez A, Alzate-Gaviria L, Chablé-Villacís R, Solís-Pereira S (2015) Laccase gene expression and vinasse biodegradation by Trametes hirsuta Strain Bm-2. Molecules 20(8):15147–15157

Tewari PK, Batra VS, Balakrishnan M (2007) Water management initiatives in sugarcane molasses based distilleries in India. Resour Conserv Recycl 52(2):351–367

Thakkar AP, Dhamankar VS, Kapadnis BP (2006) Biocatalytic decolourisation of molasses by Phanerochaete chrysosporium. Bioresour Technol 97(12):1377–1381

Thakur C, Srivastava VC, Mall ID (2009) Electrochemical treatment of a distillery wastewater: parametric and residue disposal study. Chem Eng J 148:496–505

Thiyagu R, Sivarajan P (2018) Isolation and characterization of novel bacterial strain present in a lab scale hybrid UASB reactor treating distillery spent wash. Environ Technol 15:1–7

Tiwari S, Gaur R, Singh R (2012a) Decolorization of a recalcitrant organic compound (Melanoidin) by a novel thermotolerant yeast, *Candida tropicalis* RG-9. BMC Biotechnol 12(1):30

Tiwari S, Gaur R, Rai P, Tripathi A (2012b) Decolorization of distillery effluent by thermotolerant *Bacillus subtilis*. American J Appl Sci 9(6):798–806

Tiwari S, Gaur R, Singh A (2014) Distillery Spentwash Decolorization by a Noval Consortium of *Pediococcus acidilactici* and *Candida tropicalis* under Static Condition. Pak J Biol Sci 17(6):780–791

Tondee T, Sirianutapiboon S (2008) Decolorization of molasses wastewater by *Lactobacillus plantarum* No. PV71-1861. Bioresour Technol 99(14):6258–6265

Tripathi DM, Tripathi S, Tripathi BD (2011) Implications of secondary treated distillery effluent irrigation on soil Cellulase and urease activities. J Environl Prot 2:655–661

Trivedy RK, Nakate SS (2000) Treatment of diluted distillery waste by constructed wetlands. Indian J Environ Prot 20:749–753

Valderrama LT, Del Campo CM, Rodriguez CM, Ede- Bashan L, Bashan Y (2002) Treatment of recalcitrant wastewater from ethanol and citric acid production using the microalga Chlorella vulgaris and the macrophyte *Lemna minuscula*. Water Res 36(17):4185–4192

Wagh MP, Nemade PD (2018) Biodegradation of anaerobically treated distillery spent wash by *Aspergillus* species from a distillery effluent contaminated site. Desalin Water Treat 104:234–240

Wilkie AC, Riedesel KJ, Owens JM (2000) Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks. Biomass Bioenergy 19:63–102

Wolmarans B, De Villiers G (2002) Start up of a UASB effluent treatment plant on distillery wastewater. Water SA 28(1):63–68

Wong DWS (2009) Structure and Action Mechanism of Ligninolytic Enzymes. Applied Biochemistry and Biotechnology 157 (2):174–209

Yadav S, Chandra R (2012) Biodegradation of organic compounds of molasses melanoidin (MM) from biomethanated distillery spent wash (BMDS) during the decolourisation by a potential bacterial consortium. Biodegradation 23(4):609–620

Yadav DV, Jain R, Rai RK (2010) Impact of heavy metals on sugar cane. In: Sherameti I, Varma A (eds) Soil heavy metals: soil biology series, vol 19. Springer, Berlin, pp 339–367

Zalawadia NM, Raman S (1994) Effect of distillery wastewater with graded fertilizer level on sorghum yields and soil property. J Indian Soc Soil Sci 42:575–579

Zhang M, Wang Z, Li P, Zhang H, Li X (2017) Bio-refractory dissolved organic matter and colorants in cassava distillery wastewater: characterization, coagulation treatment and mechanisms. Chemosphere 178(2017):259–267

Zhang B, Zhao H, Zhou S, Shi C, Wang C, Ni J (2009) A novel UASB−MFC−BAF integrated system for high strength molasses wastewater treatment and bioelectricity generation. Bioresour Technol (23):5687–5693

7

Integrated Approach for the Treatment of Industrial Effluent by Physico-chemical and Microbiological Process for Sustainable Environment

Komal Agrawal, Ankita Bhatt, Nisha Bhardwaj,
Bikash Kumar, and Pradeep Verma

Abstract

In the past decade, industrialisation has led to tremendous development, improving the living standards both socially and medically. However, with the increase in population and its demands, the past decade has observed an explosion of industrialisation in all the sectors. This has led to huge waste being generated and disposed of in the environment, e.g. heavy metals and effluents from distillery, paper and pulp and dye industries. Thus, various treatment methods were designed to minimise or detoxify the waste completely which included physical, chemical and microbiological. It was a gradual process where initially physical and chemical methods were used either singly or in combination. As these two techniques required huge amount of energy, chemicals and cost along with the generation of chemical waste, the interests later diverted towards the microbiological techniques, as it does not involve the use of chemical or energy and the end product formed is either less toxic or non-toxic. Thus, on the basis of the above context, the present chapter deals with various treatment strategies developed to achieve the goal of clean environment.

Keywords

Physico-chemical treatment · Biological treatment · Wastewater · Sustainable environment

---

K. Agrawal · A. Bhatt · N. Bhardwaj · B. Kumar · P. Verma (✉)
Bioprocess and Bioenergy Laboratory, Department of Microbiology, Central University of Rajasthan, Kishangarh/Ajmer, Rajasthan, India
e-mail: pradeepverma@curaj.ac.in

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_7

7.1 Introduction

Rapid industrialisation has resulted in huge amount of waste being generated by the industries which has deleterious effect on the flora, fauna and the aquatic environment. Initially the treatment of these effluents was developed which consisted of the physical, chemical or physico-chemical approach. These methods have their limitations such as economic feasibility and utilisation of chemicals for the treatment; thus, later the interest diverted towards the biological treatment methods. Bioremediation has numerous advantages over physical-chemical methods such as ecofriendliness and economic feasibility. The concept of bioremediation is based on three techniques, i.e. biochemistry, bioavailability and bioactivity (BBB). The principle of biochemistry relates to susceptibility or willingness of a contaminant to biologically transformed. Bioavailability pertains to the degree of availability of a contaminant to microorganisms and bioactivity is associated with the optimisation of biological activities (Dua et al. 2002). The bioremediation technique can be classified into two types: in situ bioremediation (ISB) and ex situ bioremediation (ESB). In situ bioremediation helps to achieve remediation by supplying nutrients and oxygen through the contaminated zones (Kumar et al. 2011); the infiltration of nutrient sources and oxygen supports the growth of microorganisms, which in turn facilitates bioremediation. On the other hand, ex situ bioremediation in contrary to the previous technique employs removal of the waste away from the source location to a different location followed by its treatment. Bioremediation techniques are gaining acceptance as the enzymes produced by the microorganisms take part in the treatment and the toxic products are converted to less-toxic compounds (Sivaperumal et al. 2017; Nikolaivits et al. 2017). Thus, considering the above concept, the present chapter focuses on the various bioremediation processes along with a focus on the various physico-chemical and biological treatments of different industrial effluents.

7.2 Categories of Bioremediation

On the basis of the method applied for waste removal and its transportation for treatment, bioremediation techniques are categorised into two categories: in situ and ex situ bioremediation.

7.2.1 In Situ Bioremediation (ISB)

ISB techniques do not involve the removal of water or soils in order to achieve remediation, it consist of supplying nutrients and oxygen through the contaminated zones (Kumar et al. 2011). This can be achieved by infiltration of water rich in nutrients, electron acceptors and oxygen in contaminated groundwater or polluted soil. This stimulates the growth of natural microbial flora, thereby enhancing the degradation of organic contaminants (Vidali 2011). Various features like cost-effectiveness and use of harmless microbes describe the wide use of ISB methods. The

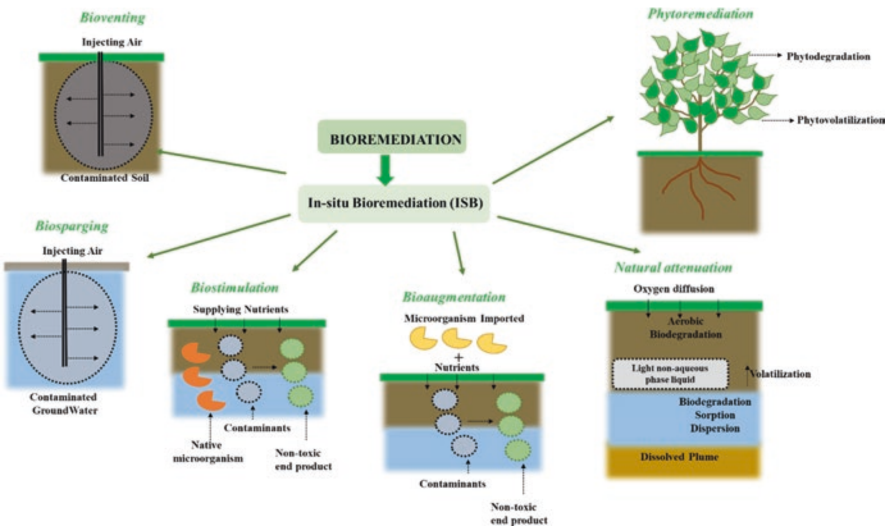


Fig. 7.1 The various types of in situ bioremediation (ISB) treatments used for the removal of the contaminants

phenomenon of chemotaxis plays a vital role in ISB because degradation of many harmful contaminants can be increased by enhancing the chemotactic abilities of microorganisms, as they can move towards the contaminants effectively (Kumar et al. 2011).

The ISB techniques are of two types, namely, “intrinsic bioremediation” and “engineered in situ bioremediation”. The former consists of enhancing the metabolic activity and thereby stimulating the indigenous microbial populations by providing continuous supply of nutrients and oxygen. On the other hand, engineered method of bioremediation pertains to the application of specific microbial populations at the polluted site. In case the site conditions become unsuitable, the engineered systems are introduced at that site. The physico-chemical conditions are further enhanced, thereby promoting microbial growth and accelerating the process of degradation. The microbial growth is also encouraged by electron acceptors, oxygen and various nutrients like nitrogen and phosphorus. The widely employed in situ treatments are (Fig. 7.1) bioventing, biosparging, biostimulation, bioaugmentation, natural attenuation and phytoremediation (Kumar et al. 2011).

7.2.1.1 Bioventing

The soil contaminated by pesticides, herbicides, fuels, semi-volatile organic compounds and non-halogenated volatile organic compounds (VOCs) are usually treated by this technology (Juwarkar et al. 2014). It is suitable for well-drained and medium or coarse textured soils (Niti et al. 2013). The bioremediation is achieved by injecting nutrients alone or in combination with oxygen in the contaminated soil (Shanahan 2004). The two frequently supplementary nutrients are nitrogen and phosphorus (Rockne and Reddy 2003). A well and a blower are the two prime components of a basic bioventing system. The air is pumped by the blower via the well and then directed in the soil (Lee et al. 2006).

7.2.1.2 Biosparging

The biosparging treatment technology is generally used for the treatment of groundwater contaminated by non-halogenated volatile organic compounds (VOCs), pesticides, herbicides, fuels, organics and semi-volatile organic compounds (SVOCs) (Juwarkar et al. 2014). In the mentioned treatment, air under pressure is injected below the water level leading to an increase in oxygen concentration of the groundwater. This further enhances the biodegradation of target contaminants by native bacterial populations. In addition, biosparging results in an increased contact between groundwater and soil by increasing the mixing in the saturated zone. A considerable amount of flexibility is entailed in the design and construction of such system. This is due to the ease and lower installation costs of small diameter points for air injection (Niti et al. 2013).

7.2.1.3 Biostimulation

The biostimulation is an ISB technique employed for treatment of subsurface regions. This is mainly employed in the treatment of groundwater and soil contaminated with non-halogenated VOCs, fuels, SVOCs, herbicides and pesticides (Juwarkar et al. 2014). Biostimulation is aimed at accumulation of various nutrients or limiting factors thereby resulting in enhancement of degradation potential of a contaminated matrix (Kadian et al. 2008). It involves the supply of aqueous solutions that are rich in electron acceptors, nutrients or other amendments. This process relies on the presence of native microorganisms that exhibit the potential to degrade the target contaminants. The process of bioremediation can be enhanced significantly by coupling the technique of biostimulation with other advanced techniques (Juwarkar et al. 2014).

7.2.1.4 Bioaugmentation

Bioaugmentation involves the import of microorganisms to the contamination site for enhancing the process of biodegradation (Niti et al. 2013). The microbes introduced include groups like bacteria, fungi, protozoa, rotifers and nematodes which have the capability to degrade various organic compounds (Juwarkar et al. 2014). This technique is usually employed along with biostimulation resulting in an increase in the activity of imported microbial populations, thereby promoting degradation (Couto et al. 2010). Various factors like inability of the introduced microbes to sustain and outcompete the native population delimit the use of bioaugmentation (Niti et al. 2013).

7.2.1.5 Natural Attenuation

The natural treatment technology is applicable for a variety of contaminants like SVOCs, fuels, non-halogenated VOCs, herbicides, pesticides, halogenated organics and high molecular weight polycyclic aromatic hydrocarbons (PAHs). It is a proactive method which is associated with the verification and monitoring of natural processes of remediation (Khan et al. 2004). This process is also known as passive, intrinsic remediation or bioattenuation and aims at employing natural processes to achieve reduction in the concentration of contaminants at target site and further containing the spread of contamination (Boparai et al. 2008; Khan et al. 2004). As soon as the contaminants get desorbed form the soil particles, they are quickly acted upon by the degraders resulting in the mineralisation of contaminants. The contaminants are thus left undisturbed during the processes of natural attenuation (Gelman and Binstock 2008). The characteristics of high molecular weight PAHs and other hydrophobic contaminants such as high sorption with soil particles and lower migration rates make them highly suitable substrates for degradation by the process of natural attenuation (Juwarkar et al. 2014). A most recent example of successful application of natural attenuation for the purpose of ISB is the recovery of Gulf of Mexico by the Deepwater Horizon blowout (Rayu et al. 2012). In this case, quick and efficient adaptation of the native microflora of deep-sea ecosystem to the oil contamination, eliminated the need for introduction of bioaugmentation with exogenous bacteria having the potential to degrade oil, members of the order *Oceanospirillales* became dominant, especially the hydrocarbon-degrading psychrophiles (Hazen et al. 2010).

7.2.1.6 Phytoremediation

Phytoremediation, also known as plant-assisted remediation, relies on using plants with or without the aid of microbes for achieving bioremediation of contaminated ecosystems. The plants employ various mechanisms for remediation, namely, phytoextraction, rhizofiltration, phytotransformation, phytovolatilisation, rhizoremediation and phytostabilisation. Phytoextraction refers to the process of uptake of contaminants by plants. These contaminants are then adsorbed to plant roots using rhizofiltration or are transformed by the enzymatic machinery of plants through phytotransformation (Juwarkar et al. 2014). They can also be volatilised by plants into the atmosphere by phytovolatilisation or degraded by the rhizosphere's microbial population via the process of rhizoremediation or incorporated to soil materials by phytostabilisation (Salt et al. 1998; Pilon-Smits 2005). This technique is employed for treatment of soil or groundwater contaminated with radionuclides, toxic heavy metals, organic contaminants such as chlorinated solvents, non-aromatic petroleum hydrocarbons and nitrotoluene ammunition wastes (Schnoor et al. 1995).

7.2.2 Ex Situ Bioremediation (ESB)

ESB technique is based upon the removal of contaminated soil or groundwater in order to achieve bioremediation. According to the state of the target contaminant, ex situ bioremediation is classified as solid-phase system or slurry-phase system (Fig. 7.2). The former includes land treatment and soil piles, while the latter consists of solid-liquid suspensions in the bioreactors (Kumar et al. 2011).

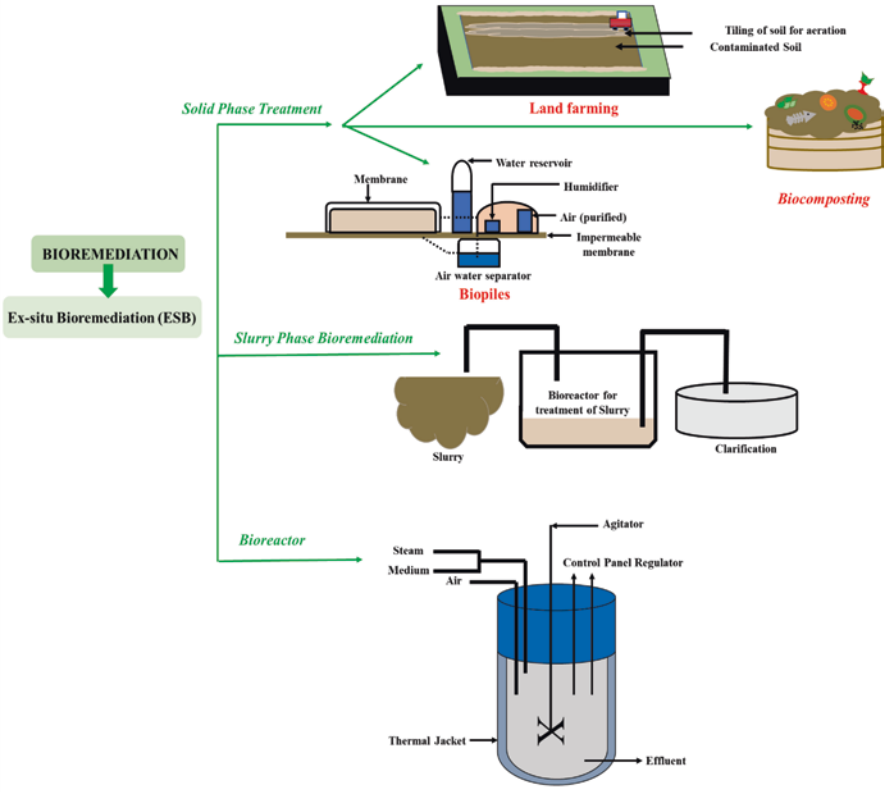


Fig. 7.2 The various types of ex situ bioremediation (ESB) treatments for the removal of the contaminants

7.2.2.1 Solid-Phase Treatment

The solid-phase treatment process consists of land farming, composting and biopiles. It includes various wastes like domestic and industrial wastes, municipal solid, agricultural wastes, sewage sludge, leaves and animal manure (Kumar et al. 2011).

7.2.2.2 Land Farming

This technique is mainly employed for treatment of soil contaminated with SVOCs, fuels, non-halogenated VOCs, herbicides, pesticides and halogenated organics. This process is aimed at stimulating the biodegradative abilities of indigenous microbial flora and further enhancing the aerobic degradation of target contaminants. It involves the excavation of contaminated soil followed by spreading it over a prepared bed which is then tilled at regular intervals until the complete degradation of contaminants is achieved. The process is primarily limited to treatment of superficial (10 cm) soil. In the case the contamination is shallow, the top layer of contaminated site does not require excavation and can be simply tilled. Land farming is widely employed and accepted as it has low monitoring and maintenance costs and clean-up steps (Juwarkar et al. 2014; Kumar et al. 2011).

7.2.2.3 Composting

The composting technique relies on the use of certain organic materials like agricultural wastes or manure that are coupled with the contaminated soil. This further encourages the development of a rich microbial population and also results in an elevated temperature characteristic of composting (Kumar et al. 2011).

7.2.2.4 Biopiles

Biopiles combine land farming and composting; surfaces contaminated with petroleum hydrocarbons are primarily treated by this process. The system consists of aerated compost piles resulting in the development of an environment favourable for the native aerobes and anaerobes. It is basically a modified version of land farming technique that is aimed at utilising leaching and volatilisation to control physical losses of the target contaminants (U.S. EPA. 1999).

7.2.2.5 Slurry-Phase Bioremediation

The slurry-phase bioremediation is a more rapid and efficient process as compared to other treatment processes. The process involves the addition of contaminated soil with water and other additives in a bioreactor. These are further mixed to enhance the contact between microbial flora of contaminated soil and target soil contaminants. Optimum conditions are developed by the supply of nutrients and oxygen to maintain and control the reactor conditions. These favour microbial growth and enhance their contaminant-degrading ability. Water is removed from the solids, and the removed water is disposed of or further treated after the completion of treatment process with a suitable technique (Kumar et al. 2011).

7.2.2.6 Bioreactors

The low permeability and heterogeneous soils are primarily treated with bioreactors. They are also employed in such cases when fast treatment methods are desired or there is difficulty in capturing the contaminated groundwater. Similar to the solid-phase ex situ treatment, toxic metabolites, e.g. vinyl chloride, can be contained in the bioreactors. The use of bioreactors is delimited by their lower cost-effectiveness as compared to solid-phase treatment methods (Juwarkar et al. 2014). Further, there is a requirement for pretreatment of contaminated soil, or an alternative method can be employed that involves the removal of the contaminant from the soil by the use of physical extraction or soil washing prior to its use and keeping in a bioreactor (U.S. EPA. 1999). Bioreactors involve the action of an engineered containment system for the processing or bioremediation of contaminated solid materials like sludge, water, sediment or soil. A slurry bioreactor is a containment vessel that is used for creating the three different phases of solid, liquid and gas. Further, the bioremediation rate of soil-bound and water-soluble contaminants is enhanced by mixing. As the contained environment in a bioreactor can be managed, controlled and thus predicted, higher biodegradation rates can be achieved in the bioreactor system (Kumar et al. 2011).

7.3 Treatment of Different Industrial Effluents by Physico-chemical and Microbiological Methods

7.3.1 Dairy Waste

There has been a rapid development in the dairy industries due to increasing demand of the dairy products, thus resulting in the generation of large amounts of wastes like dairy sludges, whey and effluents from processing, cleaning and sanitary units. These wastes are characterised by high biochemical oxygen demand (BOD), chemical oxygen demand (COD), organic load and inorganic contents and high nutrient concentrations. The different kinds of sterilizing agents, acidic and alkaline detergents are also present and demand efficient treatment techniques. The quality of air, water and soil is adversely affected by the contaminants from the dairy industry. Various physico-chemical and biological methods are employed for the treatment of the dairy industry effluents. The most efficient treatment is achieved with a combination of aerobic and anaerobic biological process (Ahmad et al. 2019).

7.3.1.1 Physico-chemical Treatment of Dairy Waste

The physico-chemical treatment of dairy waste is aimed at degradation and reduction of milk fat and protein colloids present in the effluents. Some important physico-chemical techniques widely employed are coagulation, electrocoagulation (EC) and membrane treatment (Ahmad et al. 2019). Coagulation/flocculation is used for the treatment of industrial effluents (Carvalho et al. 2013). It results in a reduction in the BOD and COD content by elimination of the organic substances present in the effluents. A significant reduction in turbidity is also attained by the decrease in number of suspended and colloidal particles. The addition of a coagulant further leads to particulate matter destabilisation and floc formation which results in sedimentation or flotation (Sarkar et al. 2006). Specific strains of lactic acid bacteria (LAB) can be used to achieve natural coagulation in the dairy effluent. These microbes cause denaturation of the milk protein by producing lactic acid from lactose fermentation. Further, COD reduction (49–82%) was achieved when chitosan was used in combination and a reduction of in COD (65–78%) was obtained when carboxymethylcellulose (CMC) was used (Dyrset et al. 1997). Further, fat removal (80%) from cheese industry effluent was achieved with a pretreatment of oxidation with ferrous sulphate ($FeSO_4$) or hydrogen peroxide (H_2O_2) (Vlyssides et al. 2012). Recently, a plant-based natural coagulant called tannin has been widely employed because of its higher efficiency with respect to other inorganic coagulants and its applicability over a wide pH range (Ahmad et al. 209).

EC is another alternative method for the treatment of dairy effluent. An anode and a cathode are the prime components of an EC unit. The supply of electric power from an external source results in oxidation of the anodic material, reduction and further deposition of elemental metals at the cathodic end. Further, a series of reactions result in the production of metal hydroxide and polyhydroxides which are responsible for removal of contaminants from effluent due to electrostatic attraction followed by coagulation (Kushwaha et al. 2011).

The membrane treatment technique for the treatment of dairy waste comprises microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), dialysis and electrodialysis (Kushwaha et al. 2011). The high-quality effluent which is suitable for immediate easy reuse is obtained by the above-mentioned technique. These processes serve as a promising alternative in cases where product recovery is a feasible option. NF is a more efficient and viable alternative to RO as the former (NF) consumes lower energy, operates at low pressure and entails higher permeate recoveries (Owen et al. 1995).

7.3.1.2 Biological Treatment of Dairy Waste

The biological treatment of dairy waste is the most efficient method for removal of organic material from dairy effluent (Carvalho et al. 2013). Various processes like aerated lagoons, trickling filters, up-flow anaerobic sludge blanket, activated sludge, sequential batch reactor and anaerobic filters are employed in the biological treatment (Yonar et al. 2018). The sequencing batch reactors (SBRs) are mainly employed for dairy effluent treatment. This is because of the effluent flexibility and wide loading capabilities associated with the SRBs (Slavov 2017). In the biological system, complex organics are transformed microbiologically, and heavy metal adsorption occurs in the presence of suitable microorganisms (Britz et al. 2006). The process of biological treatment is further categorised into aerobic and anaerobic methods.

Aerobic methods are the most widely employed method in dairy effluent treatment plants (Ahmad et al. 2019). The process relies on the activity of aerobic microorganisms responsible for the oxidation of organic compounds into carbon dioxide, water and cellular material (Britz et al2006). This is effective in the degradation of nitrogen (N) from ammonia (NH_3); however, lower efficiency is involved in the removal of phosphorus (P) which is largely determined by the environmental conditions (Slavov 2017). Certain factors like low water buffer capacity leading to rapid acidification and high lactose levels resulting in the filamentous growth of microbial flora reduce the efficiency of the process (Ahmad et al. 2019).

Anaerobic methods owing to their cost-effectiveness are more suitable than the aerobic treatment systems. Techniques like anaerobic digestion (AD), up-flow anaerobic sludge blankets (UASBs), anaerobic contact process (ACP), completely stirred tank reactor (CSTR), membrane anaerobic reactor system (MARS), expanded bed/fluidised bed or fixed bed digestors constitute the anaerobic treatment methods (Goli et al. 2019).

7.3.2 Distillery Waste

Distilleries involve the production of alcohol from molasses as the raw material using the yeast fermentation process. Two types of effluents are produced in the distilleries, namely, non-process effluent and process effluent. The former is relatively pure and thus can be recycled immediately, while the latter is comprised of spent lees, fermenter sludge and spent wash. The yeast organism *Saccharomyces cerevisiae* is the prime component of the fermenter sludge. This is recycled back to the fermentation unit with or without dilution in order to maintain the yeast concentration. On the other hand, spent lees are released form the distillation rectified column. These are further cooled appropriately and further recycled. Various physicochemical and biological treatment techniques are available for the treatment of distillery effluents. There is no individual technique for complete treatment; however, higher efficiencies are obtained in combination with physicochemical and biological methods (Sankaran et al. 2014).

7.3.2.1 Physico-chemical Treatment of Distillery Waste

These treatments are employed before or after the anaerobic method of biological treatment (Sankaran et al. 2014). The physico-chemical pretreatment or post-treatment enhances the quality of the anaerobically treated spent wash. Various pretreatment techniques like ultrasound, hydrodynamic cavitation and ozonation are coupled with biological methods for distillery effluent treatment (Sangave and Pandit 2004; Sangave et al. 2007, Siles et al. 2011, Padoley et al. 2012). A lreduction in COD (20%) was obtained when the conventional aerobic oxidation (activated sludge process) was assisted by ultrasound technique with (10,000 ppm) of initial COD concentration (Sangave et al. 2007).

7.3.2.2 Biological Treatment of Distillery Waste

The biological treatment of distillery effluent is of two types: aerobic and anaerobic methods with the (Table 7.1) highest treatment efficiencies being obtained with combination of both methods (Mohana et al. 2009). The suitability of effluent for biological treatment is indicated by its COD/BOD ratio (1.8–1.9) in narrow range (Singh et al. 2004). Aerobic treatment is used in cases of high organic load like molasses; however, the treatment is limited due to operational difficulties pertaining to bulking of sludge, higher production of biomass, operational costs, higher consumption of energy and inability to treat high BOD or COD loads in an economically feasible manner (Jiménez et al. 2003). Further, BOD:N:P (100:2.4:0.3) leads to the conclusion that anaerobic systems will be more efficient for primary treatment of the distillery effluent (Mohana et al. 2009).

The use of anaerobic methods for treatment of distillery effluent is a promising alternative that provides many advantages as compared to the conventional aerobic methods of effluent treatment (Mohana et al. 2009). The anaerobic system demands lesser energy consumption, entails production of very less amount of sludge and demonstrates high capacity for degradation of resilient contaminants. Further, the economic feasibility of this process can be enhanced by the co-production of biogas

Table 7.1 The strains reported for the decolourisation of various coloured effluents originated from different industries

Strain	Treatment (decolourisation)	Colour removal (%)	Reference
Flavodon flavus	Distillery effluent	80	Raghukumar and Rivonkar (2001)
Phanerochaete chrysosporium 1557	Distillery effluent	75	Vahabzadeh et al. (2004)
Marine basidiomycetes NIOCC	Coloured effluent	100	D'Souza et al. (2006)
Penicillium sp.	Distillery effluent	30	Jiménez et al. (2003)
Coriolus versicolor sp no. 20	Distillery effluent	34.5	Chopra et al. (2004)
Phanerochaete chrysosporium	Spent wash	53.5	Kumar et al. (1998)
Trametes versicolor	Distillery effluent	82	Benito et al. (1997)
Geotrichum candidum	Molasses effluent	80	Kim and Shoda (1999)

that finds application in various sectors (Mailleret et al. 2003). The process of AD is mostly employed for the anaerobic treatment of spent wash resulting in the production of biogas. It is a process that involves the digestion of organic compounds in the effluent by the methanogens to produce biogas, a mixture of (60%) CH_4 and (40%) CO_2. The biogas (38–40 m^3) produced form (1 m^3) spent wash (Sankaran et al. 2014). The treated effluent, i.e. the treated spent wash, and the digested sludge are other products of anaerobic digestor. The treated spent wash demands further treatment using physico-chemical techniques, whereas the sludge is used as a manure. The treatment of inorganic contaminants and removal of colour are the major challenges associated with anaerobically digested spent wash (ADSW). This can be overcome by employing other physico-chemical or biological methods in combination with AD process (Sankaran et al. 2014).

The technique of phycoremediation is also employed for further treatment of ADSW. This relies on the utilisation of microalgae for treatment purposes. The cultivation of microalgae in ADSW exhibits various advantages like nutrients needed for algal growth are already present in the effluent, further supply of water for growth is not required and the obtained algal biomass can be further employed for production of a variety of biofuels (Sankaran et al. 2014).

7.3.3 Paper and Pulp Waste

The paper and pulp industry uses and produces huge amount of biomass-based energy and materials. The paper and pulp industries generate large amounts of effluents that can adversely affect the environment and, thus, demand proper treatment before being disposed of or reused (Svensson and Berntsson 2014). Depending upon the employed raw materials and the production process, the generated effluents are characterised by high COD and low biodegradability and consists of approximately seven hundred (~700) organic and inorganic compounds (Karrasch et al. 2006).

7.3.3.1 Physico-chemical Treatment of Paper and Pulp Waste

The suspended or floating matters and toxic substances are removed from the effluent using various methods of physicochemical treatment like coagulation and precipitation, reverse osmosis, sedimentation and floatation, filtration, wet oxidation, adsorption, ozonation and advanced oxidation processes. Coagulation and precipitation method depend on generation of larger flocs from small particles by addition of metal salts into the effluent stream. According to Wang et al. (2011), 95.7% was removal efficieny of turbidity, 83.4% was removal efficiency of lignin and 72.7% water recovery was obtained by employing 871 mg/L aluminium chloride as the coagulant, 22.3 mg/L natural polymer (starch-g-PAM-g-PDMC; polyacrylamide and poly (2-methacryloyloxyethyl) trimethyl ammonium chloride) as flocculant at pH 8.35 for purpose of treatment in the primary sedimentation tank (Kamali and Khodaparast 2015).

Electrochemical methods, in contrast to the physicochemical treatment techniques, are more economically and technically feasible in large-scale operations (Soloman et al. 2009). These electrochemical methods are highly efficient in the treatment of high molecular weight dissolved organic contaminants (Lewis et al. 2013).

The paper and pulp industry effluent can be treated by the technique of reverse osmosis (Kamali and Khodaparast 2015). This process also has the potential to destroy pathogens (Asano and Cotruvo 2004). However, its use is limited due to some technical and economical limitations with respect to retentate disposal (Greenlee et al. 2010). The utilisation of appropriate pretreatment techniques enhances the efficiency of RO systems (Kamali and Khodaparast 2015).

7.3.3.2 Biological Treatment of Paper and Pulp Waste

As compared to physico-chemical treatment methods, biological treatment is eco-friendly, cost-effective and well suitable for COD/BOD reduction from waste effluent (Kamali and Khodaparast 2015). These processes are based on the utilisation of bacteria, fungi, algae and enzymes alone or in combination with other physico-chemical methods (Singhal and Thakur 2009). The commonly available biological treatments are activated sludge process, stabilisation ponds and anaerobic lagoons (Tiku et al. 2010].

Activated sludge treatment and aerated lagoons constitute the conventional methods of aerobic treatment. These processes results in the microbial conversion of organic matter into carbon dioxide and water with the microbial growth being sustained by aerobic respiration (Virkutyte 2017).

Activated sludge process (ASP) is highly cost efficient and is (Dykstra et al. 2014, 2015) primarily used for the removal of suspended solids (SS), BOD, COD, chlorinated phenols, catechols, 1,1-dichlorodimethyl sulfone, guaiacols, chlorinated acetic acid and vanillins (Virkutyte 2017). ASP depends on the degradation of target organic contaminants by certain microbial populations which further results in the production of high-quality effluent. The microbial growth, attachment and floc formation is the basic principle governing the ASP process. These formed flocs settles to the bottom of the treatment tank, thereby, resulting a liquid free from suspended solids and organic matter (Gernaey et al. 2004; Adav et al. 2008; Chan et al. 2009; Mahmood and Elliott 2006).This screened effluent is then mixed with a known amount of recycled liquid and microorganisms which is introduced from a secondary clarifying tank. The resulting mixture called mixed liquor is further stirred in presence of air and transferred to a clarifier where majority of the microbial population settles while the remaining effluent is sent for further treatment. The settled solids called the activated sludge is then returned back to the first tank and the entire cycle is repeated (Virkutyte 2017).

The aerated lagoons (ALs) provide shelter to diverse and complex microbial populations which are primarily governed by the physico-chemical parameters of the effluent, prevalent environmental conditions and operational characteristics of the lagoon. The degradation of contaminants and their transformation to carbon dioxide and water is achieved by the activity and stability of the microbial communities present in ALs. However, changes in environmental conditions, variations in influent pH, temperature, organic loading rates and toxic compound levels as well as seasonal climate changes have a profound effect on the composition and performance of these microorganisms (Virkutyte 2017). Further, the efficiency of the process is determined by operational conditions, design of the system and type of effluent (Mehmood et al. 2009; Welander et al. 1997).

7.3.4 Refinery and Petrochemical Waste

The various types of pollutants generated from the refineries and petrochemical industries included nutrients, refractory organics, volatile organic compounds, heavy metals, dissolved inorganic solids and biological pathogens which are characterised in the form of COD, BOD, TOC and TSS. The physical and chemical methods are not efficient for the complete removal of oil and suspended solids thus secondary and tertiary treatments (e.g. membrane separation, biological treatment, EC, ozonation, advanced oxidation process, adsorption, ion exchange, coagulation and hybrid technologies) are employed for the removal of organic substances in order to make the effluent suitable (~99% removal) enough to be discharged in the environment (Diya'uddeen et al. 2011; Ranade and Bhandari 2014; Santos et al. 2015; El-Naas et al. 2014; Hami et al. 2007; El-Naas et al. 2016).

7.3.4.1 Physico-chemical Treatment of Refinery and Petrochemical Waste

The American Petroleum Institute (API) gravitational oil separators, corrugated plate interceptors (CPI) and parallel plate interceptors (PPI) removes free oil and suspended solids. The API separator in spite of occupying large surface area has more utility in comparison to the CPI and PPI as it has three phase separators for removing oils, solids and water, whereas the CPI and PPI are two-phase separators to remove oil and water (Diya'uddeen et al. 2011).

Sedimentation is used to remove flocs and suspended solids which after a certain period of time and under inert conditions helps in the separation of precipitated solids and waste (Krishna et al. 2017).

Dissolved air flotation (DAF) has an advantage over gravity-based separators as this method removes oil/water emulsions. This technique involves dissolving compressed oil present in the wastewater under pressure which results in the formation of small air bubbles (i.e., suspended solids and oil droplet). These air bubbles with the release in pressure lift the waste to surface which are then removed by DAF (Mohr and Jenks 1998; Karhu et al. 2014).

Electrodialysis is mainly used to reduce the salinity and concentration of dissolved solids. It involves the separation of cations and anions present in the wastewater by placing the membrane between the two electrodes (Fakhru'l-Razi et al. 2009; Krishna et al. 2017).

7.3.4.2 Biological Treatment of Refinery and Petrochemical Waste

The biological treatment process can be of two types, the first being suspended growth processes where the microorganisms are suspended in the wastewater and the organic substances are utilised as the food sources by the microorganisms. The second method involves the use of attached growth processes/fixed-film processed in which the microorganisms are attached to inert media thereby generating biofilm which in turn comes in contact with wastewater and oxygen (Jafarinejad 2017a, 2017b).

7.3.5 Pharmaceutical Waste

The waste generated by the pharmaceutical industries has fluctuation in terms of its composition and quantity which depends upon the raw material used by the industry, season and time of the manufacturing unit producing various pharmaceutical products (Gadipelly et al. 2014).

7.3.5.1 Physico-chemical Treatment of Pharmaceutical Waste

The various physico-chemical processes are applied for the treatment of pharmaceutical waste such as microfiltration, ultra-filtration, nanofiltration, reverse osmosis, electrodialysis reversal and membrane bioreactors (Bellona and Drewes 2007; Snyder et al. 2007). The pore size of the membrane creates problem with the treatment of wastewater, as micropollutants can pass through the membrane. Thus, reverse osmosis has been used effectively for the treatment of drinking water (Watkinson et al. 2007). Activated carbon (AC) is the most conventional technology for the removal of both synthetic and natural wastes, where the AC can be used in both powdered and granular form, packed in the bed filter (Annesini et al. 1987).

7.3.5.2 Biological Treatment of Pharmaceutical Waste

The aerobic treatment method has been effectively used to treat various pharmaceutical wastewaters (El-Gohary et al. 1995). However, the conventional activated sludge use depends on two parameters i.e. temperature and the hydraulic retention time (HRT). On the other hand, the membrane bioreactor has been gaining attention due to its economic feasibility, high sludge retention time (SRT) and lastly effective separation of suspended solids in the presence of the membranes (Urase et al. 2005). The other biological treatment method involves anaerobic treatment, e.g. continuous stirred tank reactors (anaerobic digestion), fluidised bed reactor, etc. (Sponza and Çelebi 2012; Oktem et al. 2008). The main advantage of the anaerobic system over the aerobic system includes its efficiency to deal with high wastewater concentrations with low energy involvement, economic feasibility along with the recovery of biomethane which can be used as a valued energy source (Deegan et al. 2011).

7.3.6 Palm Oil Mill Effluents (POME)

The POME consists of soluble waste above the threshold level in the form of solid, liquid or gas (e.g. methane) (Igwe and Onyegbado, 2007), and various treatment methods employed are:

7.3.6.1 Physico-chemical Treatment of Palm Oil Mill Effluent

The various physico-chemical treatments involve the use of coagulation-flocculation, which gives good results by filtering suspended solids. On the other hand, photocatalytic reaction involves the use of TiO_2 (most commonly studied), and it efficiently mineralises and disinfects the organic compounds and the pathogenic microorganism, respectively (Zheng et al. 2017; Chong et al. 2010). Lastly, cavitation is a three-step process where the bubbles form, grow and then collapse due to sound waves travelling in alternate fashion of compression and rarefaction through the liquid (Gallipoli and Braguglia 2012). It can be of four types, i.e. acoustic (ultrasound), hydrodynamic, optic and particle cavitation, and only ultrasound (passage of very high frequency of sound waves) and hydrodynamic cavitation (liquid is passed through a constriction such as an orifice or venture) have been applied for the treatment of the wastewater (Jyoti and Pandit 2001; Parthasarathy et al. 2016; Bagal and Gogate 2014).

7.3.6.2 Biological Treatment of Palm Oil Mill Effluents

The anaerobic digestion can effectively treat high concentration of carbon present in POME (Wu et al. 2010) with effective reduction in greenhouse gas (GHG) emission, source of biogas producing a mixture of carbon dioxide and methane (Raposo et al. 2012; Lam and Lee 2011). Other anaerobic methods were also developed due to its advantages which include anaerobic suspended growth processes, immobilised cell bioreactors, anaerobic filter, up-flow anaerobic sludge blanket reactors, etc. Microbial fuel cell (MFC) has also been used to treat POME which converts organic-rich wastewater into electrical energy with the help of microorganisms (Cheng et al.

2010). Both single-chambered MFC and double-chambered MFC have been utilised; however, the single-chambered MFC did not give satisfying results due to issues in the reactor design or the parameters (Islam et al. 2016); therefore later MFC (two-stage) coupled with immobilised biological aerated filter (I-BAF) was proposed (Cheng et al. 2010). Vermicomposting is a process where earthworms are employed for the biodegradation of the organic waste into "humus-like vermicast" (Hussain and Abbasi 2018) and exhibits higher degradation as compared to other conventional treatment processes.

7.3.7 Tannery Wastewater

The tannery wastewater consists of organic, inorganic, nitrogenous, chromium, sulphides, suspended solids and dissolved solids; however, tannery waste varies from industry to industry. Various treatment techniques applied for the treatment include the following.

7.3.7.1 Physico-chemical Treatment of Tannery Wastewater

The method of coagulation or flocculation has been applied for the treatment of the tannery waste, e.g. aluminium sulphate ($AlSO_4$) and ferric chloride ($FeCl_3$) (Lofrano et al. 2006). Recently, the efficiency of the coagulant was improved by the use of polyaluminium chloride (PAC), polyaluminium silicate (PASiC) and polyaluminium ferric chloride (PAFC). Advanced oxidation processes have been used to treat the tannery waste by using O_3 and H_2O_2 as oxidising agents or Fe, Mn and TiO_2 as catalyst either in the presence or absence of UV light (Schrank et al. 2004). In addition to the above methods, Fenton and ozone-based processes and electrochemical processes have also been applied.

7.3.7.2 Biological Treatment of Tannery Wastewater

Both aerobic and anaerobic processes have been applied for the treatment of waste. In the case of aerobic system, the SBR has been more preferred as it carries out reactions like nitrification and denitrification (Ganesh et al. 2006), whereas in anaerobic process anaerobic filters (AF) consisting of up-flow anaerobic filters and down-flow anaerobic filters and up-flow anaerobic sludge blanket reactors (Lefebvre et al. 2006; El-Sheikh et al. 2011) are used. Membrane bioreactors are also used which have advantages such as elimination of settling basins, independence of process performance from filamentous bulking or other phenomena affecting settleability (Munz et al. 2008; Suganthi et al. 2013). In addition, hybrid treatment technologies have also been used which consist of combination of treatments, e.g. biological treatment can be used to remove COD followed by ozonation, thereby increasing the biodegradation of the organic compounds (Dogruel et al. 2006; Di Iaconi et al. 2010; Di Iaconi 2012; Houshyar et al. 2012).

7.3.8 Textile Waste

The textile effluent consists of acids, alkalis, dyes, hydrogen peroxide, starch, surfactants dispersing agents and soaps of metals (Paul et al. 2012) along with aromatic and heterocyclic dyes which are used in the industry. They exhibit high BOD, COD, total dissolved solid (TDS) and total suspended solid (TSS) which pollute the environment. The colour imparted by the dye diminished light penetration in water bodies, thereby hampering the development of aquatic organisms. Thus, the treatment of the effluents has been done using various physical, chemical, biochemical treatments either single or in combination.

7.3.8.1 Physico-chemical Treatment of Textile Waste

Coagulation/flocculation is used to remove disperse dyes efficiently with low decolourisation with reactive and vat dyes (Yeap et al. 2014). Adsorption and activated carbon have been used for the decolourisation of various dyes. Adsorbents such as charcoal, date stones and potato plant waste have also been used for the decolourisation of the dyes; however, the supply of these products and their dumping and high cost are the main limitations associated with the process. The oxidation-based method has been applied for the degradation of the dye effluent, pesticide either partly or completely under optimal conditions. The advanced oxidation process involves the use of oxidation and Fenton chemistry. In addition, the microfiltration technique has also been used for the removal of particles and colloidal dye. However, the un-consumed auxiliary chemicals, dissolved organic pollutants and other soluble contaminants escape from the membrane (Juang et al. 2013; Koltuniewicz and Drioli 2008), thereby restricting its utility for the treatment of dye. In addition, ultrafiltration, nanofiltration, EC (Table 7.2) and reverse osmosis have also been used for the treatment of wastewater.

Table 7.2 The dye removal efficiency using electrocoagulation of various types of wastewater generated by dye industry

Wastewater	Current/current density	Dye removal (%)	References
Azo, anthraquinone, xanthene	0.3 A	98	Wei et al. (2012)
Indigo carmine	54.57 A/m^2	100	Secula et al. (2012)
Bomaplex red CR-L	0.50 mA/cm^2	99.1	Yildiz (2008)
Levafix blue CA	35.5 mA/cm^2	99.5	Korbahti and Tanyolac (2008)
Reactive blue 19	21.66 mA/cm^2	100	Rajkumar et al. (2007)
Reactive blue 19, acid red 266, disperse yellow 218	1.6 A	98	Yang and McGarrahan (2005)
Acid red 14	80 A/m^2	93	Daneshvar et al. (2004)
Disperse red	20.8 mA/cm^2	95	Merzouk et al. (2011)

7.3.8.2 Biological Treatment of Textile Waste

The biological treatment methods involve bacteria, fungi and algae and have numerous advantages over other methods such as they are ecofriendly, economically feasible and non-hazardous (Hayat et al., 2015). The fungal cultures that produce enzymes such as lignin peroxidase, manganese peroxidase and laccase (Chander, 2014) can effectively degrade various types of dyes. Algal cultures have also been used which involve three steps in the treatment of textile dyes, first consumption, second transformation and lastly chromophores adsorption on algae. As per Khataee et al. (2011), the green macroalgae *Cladophora* species have capability to degrade mainly azo dyes due to presence of azo-reductase enzymes. In addition to pure microbial culture's, consortia of bacterial cultures are effectively used as they can act conjointly to biodegrade the waste (Saroj et al. 2015). In addition to the above methods, microbial fuel cell (MFC) (Pant et al. 2010) and phytoremediation (Kagalkar et al. 2009) have also been employed.

7.4 Limitations and Future Prospects

There are certain limitations associated with bioremediation, where the treatment might only be restricted to biodegradable components and not all compounds treated can be harmless; in certain cases the end products are more toxic than the parent compound. In the biological system, appropriate levels of nutrients along with contaminants and metabolically active microorganisms must be used. The application of bioremediation at field scale is difficult and the treatment time is also long. However, the process of bioremediation has gained acceptance over the other physical and chemical treatment processes as the residues produced after the biological treatment are usually harmless consisting of CO_2, H_2O and cell biomass. The complete degradation of the contamination on site is possible which prevents the transport of the contaminants without the disruption of normal activities, and lastly it is economically feasible and ecofriendly (Kumar et al. 2011).

7.5 Conclusion

The advancement of technology and industrialisation have imposed severe pressure upon the environment globally. Thus, in an attempt to treat pollutants, various techniques were developed, and at present biological treatment is the most accepted process worldwide. This approach not only degrades the pollutant on-site but is also economically feasible and sustainable at the same time, thereby contributing towards a clean environment.

References

Adav SS, Lee DJ, Show KY, Tay JH (2008) Aerobic granular sludge: recent advances. Biotechnol Adv. https://doi.org/10.1016/j.biotechadv.2008.05.002

Ahmad T, Aadil RM, Ahmed H, ur Rahman U, Soares BC, Souza SL, Pimentel TC, Scudino H, Guimarães JT, Esmerino EA, Freitas MQ (2019) Treatment and utilization of dairy industrial waste: a review. Trends Food Sci Technol. https://doi.org/10.1016/j.tifs.2019.04.003

Annesini MC, Gironi F, Ruzzi M, Tomei C (1987) Adsorption of organic compounds onto activated carbon. Water Res. https://doi.org/10.1016/0043-1354(87)90065-0

Asano T, Cotruvo JA (2004) Groundwater recharge with reclaimed municipal wastewater: health and regulatory considerations. Water Res 38(8):1941–1951. https://doi.org/10.1016/j.watres.2004.01.023

Bagal MV, Gogate PR (2014) Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: a review. Ultrason Sonochem. https://doi.org/10.1016/j.ultsonch.2013.07.009

Bellona C, Drewes JE (2007) Viability of a low-pressure nanofilter in treating recycled water for water reuse applications: a pilot-scale study. Water Res. https://doi.org/10.1016/j.watres.2007.05.0

Benito GG, Miranda MP, De Los Santos DR (1997) Decolorization of wastewater from an alcoholic fermentation process with Trametes versicolor. Bioresour Technol. https://doi.org/10.1016/S0960-8524(97)84695-0

Boparai HK, Shea PJ, Comfort SD, Machacek TA (2008) Sequencing zerovalent iron treatment with carbon amendments to remediate agrichemical-contaminated soil. Water Air Soil Pollut. https://doi.org/10.1007/s11270-008-9682-3

Britz TJ, Van Schalkwyk C, Hung YT (2006) Treatment of dairy processing wastewaters. Waste treatment in the food processing industry Boca Raton : Taylor & Francis:1–28

Carvalho F, Prazeres AR, Rivas J (2013) Cheese whey wastewater: characterization and treatment. Sci Total Environ. https://doi.org/10.1016/j.scitotenv.2012.12.038

Chan YJ, Chong MF, Law CL, Hassell DG (2009) A review on anaerobic–aerobic treatment of industrial and municipal wastewater. Chem Eng J. https://doi.org/10.1016/j.cej.2009.06.041

Chander M (2014) Bioremediation of industrial effluents using some white rot Fungi. LAP LAMBERT. Academic Publishing, Saarbrücken

Cheng J, Zhu X, Ni J, Borthwick A (2010) Palm oil mill effluent treatment using a two-stage microbial fuel cells system integrated with immobilized biological aerated filters. Bioresour Technol. https://doi.org/10.1016/j.biortech.2009.12.017

Chong MN, Jin B, Chow CW, Saint C (2010) Recent developments in photocatalytic water treatment technology: a review. Water Res. https://doi.org/10.1016/j.watres.2010.02.039

Chopra P, Singh D, Verma V, Puniya AK (2004) Bioremediation of melanoidin containing digested spentwash from cane-molasses distillery with white rot fungus *Coriolus versicolor*. Indian J Microbiol:44, 197–200

Couto MN, Monteiro E, Vasconcelos MT (2010) Mesocosm trials of bioremediation of contaminated soil of a petroleum refinery: comparison of natural attenuation, biostimulation and bioaugmentation. Environ Sci Pollut Res. https://doi.org/10.1007/s11356-010-0318-y

D'Souza DT, Tiwari R, Sah AK, Raghukumar C (2006) Enhanced production of laccase by a marine fungus during treatment of colored effluents and synthetic dyes. Enzym Microb Technol. https://doi.org/10.1016/j.enzmictec.2005.07.005

Daneshvar N, Sorkhabi HA, Kasiri MB (2004) Decolorization of dye solution containing acid red 14 by electrocoagulation with a comparative investigation of different electrode connections. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2004.03.021

Deegan AM, Shaik B, Nolan K, Urell K, Oelgemöller M, Tobin J, Morrissey A (2011) Treatment options for wastewater effluents from pharmaceutical companies. Int J Environ Sci Technol. https://doi.org/10.1007/BF03326250

Di Iaconi C (2012) Biological treatment and ozone oxidation: integration or coupling? Bioresour Technol. https://doi.org/10.1016/j.biortech.2011.12.007

Di Iaconi C, Del Moro G, De Sanctis M, Rossetti S (2010) A chemically enhanced biological process for lowering operative costs and solid residues of industrial recalcitrant wastewater treatment. Water Res. https://doi.org/10.1016/j.watres.2010.04.017

Diya'uddeen BH, Daud WM, Aziz AA (2011) Treatment technologies for petroleum refinery effluents: A review. Process Saf Environ Prot. https://doi.org/10.1016/j.psep.2010.11.003

Dogruel S, Genceli EA, Babuna FG, Orhon D (2006) An investigation on the optimal location of ozonation within biological treatment for a tannery wastewater. J Chem Technol Biotechnol. https://doi.org/10.1002/jctb.1620

Dua M, Singh A, Sethunathan N, Johri A (2002) Biotechnology and bioremediation: successes and limitations. Appl Microbiol Biotechnol. https://doi.org/10.1007/s00253-002-1024-6

Dykstra CM, Giles HD, Banerjee S, Pavlostathis SG (2014) Biotransformation of phytosterols under aerobic conditions. Water Res. https://doi.org/10.1016/j.watres.2014.03.062

Dykstra CM, Giles HD, Banerjee S, Pavlostathis SG (2015) Fate and biotransformation of phytosterols during treatment of pulp and paper wastewater in a simulated aerated stabilization basin. Water Res. https://doi.org/10.1016/j.watres.2014.10.030

Dyrset N, Lystad KQ, Levine DW (1997) Development of a fermentation process for production of a κ-carrageenase from Pseudomonas carrageenovora. Enzym Microb Technol. https://doi.org/10.1016/S0141-0229(96)00169-X

El-Gohary FA, Abou-Elela SI, Aly HI (1995) Evaluation of biological technologies for wastewater treatment in the pharmaceutical industry. Water Sci Technol. https://doi.org/10.1016/0273-1223(96)00112-6

El-Naas MH, Alhaija MA, Al-Zuhair S (2014) Evaluation of a three-step process for the treatment of petroleum refinery wastewater. J Environ Chem Eng. https://doi.org/10.1016/j.jece.2013.11.024

El-Naas MH, Surkatti R, Al-Zuhair S (2016) Petroleum refinery wastewater treatment: A pilot scale study. J Water Process Eng. https://doi.org/10.1016/j.jwpe.2016.10.005

El-Sheikh MA, Saleh HI, Flora JR, AbdEl-Ghany MR (2011) Biological tannery wastewater treatment using two stage UASB reactors. Desalination. https://doi.org/10.1016/j.desal.2011.03.060

Fakhru'l-Razi A, Pendashteh A, Abdullah LC, Biak DR, Madaeni SS, Abidin ZZ (2009) Review of technologies for oil and gas produced water treatment. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2009.05.044

Gadipelly C, Pérez-González A, Yadav GD, Ortiz I, Ibáñez R, Rathod VK, Marathe KV (2014) Pharmaceutical industry wastewater: review of the technologies for water treatment and reuse. Ind Eng Chem Res. https://doi.org/10.1021/ie501210j

Gallipoli A, Braguglia CM (2012) High-frequency ultrasound treatment of sludge: combined effect of surfactants removal and floc disintegration. Ultrason Sonochem. https://doi.org/10.1016/j.ultsonch.2011.12.014

Ganesh R, Balaji G, Ramanujam RA (2006) Biodegradation of tannery wastewater using sequencing batch reactor—respirometric assessment. Bioresour Technol. https://doi.org/10.1016/j.biortech.2005.09.003

Gelman F, Binstock R (2008) Natural attenuation of MTBE and BTEX compounds in a petroleum contaminated shallow coastal aquifer. Environ Chem Lett. https://doi.org/10.1007/s10311-007-0125-y

Gernaey KV, van Loosdrecht MC, Henze M, Lind M, Jørgensen SB (2004) Activated sludge wastewater treatment plant modelling and simulation: state of the art. Environ Model Softw. https://doi.org/10.1016/j.envsoft.2003.03.005

Goli A, Shamiri A, Khosroyar S, Talaiekhozani A, Sanaye R, Azizi K (2019) A review on different aerobic and anaerobic treatment methods in dairy industry wastewater. J Environ Treat Tech

Greenlee LF, Testa F, Lawler DF, Freeman BD, Moulin P (2010) Effect of antiscalants on precipitation of an RO concentrate: metals precipitated and particle characteristics for several water compositions. Water Res 44(8):2672–2684. https://doi.org/10.1016/j.watres.2010.01.034

Hami ML, Al-Hashimi MA, Al-Doori MM (2007) Effect of activated carbon on BOD and COD removal in a dissolved air flotation unit treating refinery wastewater. Desalination. https://doi.org/10.1016/j.desal.2007.01.003

Hayat H, Mahmood Q, Pervez A, Bhatti ZA, Baig SA (2015) Comparative decolorization of dyes in textile wastewater using biological and chemical treatment. Sep Purif Technol. https://doi.org/10.1016/j.seppur.2015.09.025

Hazen TC, Dubinsky EA, DeSantis TZ, Andersen GL, Piceno YM, Singh N, Jansson JK, Probst A, Borglin SE, Fortney JL, Stringfellow WT (2010) Deep-sea oil plume enriches indigenous oil-degrading bacteria. Science. https://doi.org/10.1126/science.1195979

Houshyar Z, Khoshfetrat AB, Fatehifar E (2012) Influence of ozonation process on characteristics of pre-alkalized tannery effluents. Chem Eng J. https://doi.org/10.1016/j.cej.2012.02.053

Hussain N, Abbasi S (2018) Efficacy of the vermicomposts of different organic wastes as “clean” fertilizers: state-of-the-art. Sustainability. https://doi.org/10.3390/su10041205

Igwe JC, Onyegbado CC (2007) A review of palm oil mill effluent (POME) water treatment. Global J Environ Res. https://pdfs.semanticscholar.org/1e05/fb0131d39e3048c846d4b-97450c5e7dfa761.pdf

Islam MA, Rahman M, Yousuf A, Cheng CK, Wai WC (2016) Performance of Klebsiella oxytoca to generate electricity from POME in microbial fuel cell. In: MATEC web of conferences, vol 38. EDP Sciences, p 03004. https://doi.org/10.1051/matecconf/20163803004

Jafarinejad S (2017a) Petroleum waste treatment and pollution control, Butterworth-Heinemann is an imprint of Elsevier. Cambridge MA, Oxford

Jafarinejad S (2017b) Oil-spill response. In: Petroleum waste treatment and pollution control. Elsevier

Jiménez AM, Borja R, Martın A (2003) Aerobic–anaerobic biodegradation of beet molasses alcoholic fermentation wastewater. Process Biochem. https://doi.org/10.1016/S0032-9592(02)00325-4

Juang Y, Nurhayati E, Huang C, Pan JR, Huang S (2013) A hybrid electrochemical advanced oxidation/microfiltration system using BDD/Ti anode for acid yellow 36 dye wastewater treatment. Sep Purif Technol. https://doi.org/10.1016/j.seppur.2013.09.042

Juwarkar AA, Misra RR, Sharma JK (2014) Recent trends in bioremediation. In: Geomicrobiology and biogeochemistry. Springer, Berlin/Heidelberg. https://doi.org/10.1007/978-3-642-41837-2_5

Jyoti KK, Pandit AB (2001) Water disinfection by acoustic and hydrodynamic cavitation. Biochem Eng J. https://doi.org/10.1016/S1369-703X(00)00128-5

Kadian N, Gupta A, Satya S, Mehta RK, Malik A (2008) Biodegradation of herbicide (atrazine) in contaminated soil using various bioprocessed materials. Bioresour Technol. https://doi.org/10.1016/j.biortech.2007.06.064

Kagalkar AN, Jagtap UB, Jadhav JP, Bapat VA, Govindwar SP (2009) Biotechnological strategies for phytoremediation of the sulfonated azo dye direct red 5B using Blumea malcolmii hook. Bioresour Technol. https://doi.org/10.1016/j.biortech.2009.03.049

Kamali M, Khodaparast Z (2015) Review on recent developments on pulp and paper mill wastewater treatment. Ecotoxicol Environ Saf. https://doi.org/10.1016/j.ecoenv.2014.05.005

Karhu M, Leiviskä T, Tanskanen J (2014) Enhanced DAF in breaking up oil-in-water emulsions. Sep Purif Technol. https://doi.org/10.1016/j.seppur.2013.11.007

Karrasch B, Parra O, Cid H, Mehrens M, Pacheco P, Urrutia R, Valdovinos C, Zaror C (2006) Effects of pulp and paper mill effluents on the microplankton and microbial self-purification capabilities of the Biobio River, Chile. Sci Total Environ. https://doi.org/10.1016/j.scitotenv.2005.03.029

Khan FI, Husain T, Hejazi R (2004) An overview and analysis of site remediation technologies. J Environ Manag. https://doi.org/10.1016/j.jenvman.2004.02.003

Khataee AR, Dehghan G, Zarei M, Ebadi E, Pourhassan M (2011) Neural network modeling of biotreatment of triphenylmethane dye solution by a green macroalgae. Chem Eng Res Des. https://doi.org/10.1016/j.cherd.2010.05.009

Kim SJ, Shoda M (1999) Batch decolorization of molasses by suspended and immobilized fungus of Geotrichum candidum Dec 1. J Biosci Bioeng. https://doi.org/10.1016/S1389-1723(00)87682-3

Kołtuniewicz A, Drioli E (2008) Membranes in clean technologies. Wiley-VCH

Körbahti BK, Tanyolaç A (2008) Electrochemical treatment of simulated textile wastewater with industrial components and Levafix blue CA reactive dye: optimization through response surface methodology. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2007.06.010

Krishna IM, Manickam V, Shah A, Davergave N (2017) Environmental management: science and engineering for industry. Butterworth-Heinemann

Kumar V, Wati L, Nigam P, Banat IM, Yadav BS, Singh D, Marchant R (1998) Decolorization and biodegradation of anaerobically digested sugarcane molasses spent wash effluent from biomethanation plants by white-rot fungi. Process Biochem. https://doi.org/10.1016/S0032-9592(97)00047-2

Kumar A, Bisht BS, Joshi VD, Dhewa T (2011) Review on bioremediation of polluted environment: a management tool. Int J Environ Sci. http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.422.2461&rep=rep1&type=pdf

Kushwaha JP, Srivastava VC, Mall ID (2011) An overview of various technologies for the treatment of dairy wastewaters. Crit Rev Food Sci Nutr. https://doi.org/10.1080/10408

Lam MK, Lee KT (2011) Renewable and sustainable bioenergies production from palm oil mill effluent (POME): win–win strategies toward better environmental protection. Biotechnol Adv. https://doi.org/10.1016/j.biotechadv.2010.10.001

Lee TH, Byun IG, Kim YO, Hwang IS, Park TJ (2006) Monitoring biodegradation of diesel fuel in bioventing processes using in situ respiration rate. Water Sci Technol. https://doi.org/10.2166/wst.2006.131

Lefebvre O, Vasudevan N, Torrijos M, Thanasekaran K, Moletta R (2006) Anaerobic digestion of tannery soak liquor with an aerobic post-treatment. Water Res. https://doi.org/10.1016/j.watres.2006.02.004

Lewis R, Nothrop S, Chow CW, Everson A, van Leeuwen JA (2013) Colour formation from pre and post-coagulation treatment of Pinus radiata sulfite pulp mill wastewater using nutrient limited aerated stabilisation basins. Sep Purif Technol DOI: https://doi.org/10.1016/j.seppur.2013.04.022

Lofrano G, Belgiorno V, Gallo M, Raimo A, Meric S (2006) Toxicity reduction in leather tanning wastewater by improved coagulation flocculation process. Global NEST J. https://journal.gnest.org/sites/default/files/Journal%20Papers/151-158_LOFRANO_386_8-2.pdf

Mahmood T, Elliott A (2006) A review of secondary sludge reduction technologies for the pulp and paper industry. Water Res. https://doi.org/10.1016/j.watres.2006.04.001

Mailleret L, Bernard O, Steyer JP (2003) Robust regulation of anaerobic digestion processes. Water Sci Technol 48(6):87–94. https://doi.org/10.2166/wst.2003.0364

Mehmood MK, Adetutu E, Nedwell DB, Ball AS (2009) In situ microbial treatment of landfill leachate using aerated lagoons. Bioresour Technol. https://doi.org/10.1016/j.biortech.2008.11.031

Merzouk B, Gourich B, Madani K, Vial C, Sekki A (2011) Removal of a disperse red dye from synthetic wastewater by chemical coagulation and continuous electrocoagulation. A comparative study. Desalination. https://doi.org/10.1016/j.desal.2011.01.029

Mohana S, Acharya BK, Madamwar D (2009) Distillery spent wash: treatment technologies and potential applications. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2008.06.079

Mohr KS, Jenks OK (1998) Effective pretreatment for hydrocarbon/VOC removal

Munz G, Gori R, Cammilli L, Lubello C (2008) Characterization of tannery wastewater and biomass in a membrane bioreactor using respirometric analysis. Bioresour Technol. https://doi.org/10.1016/j.biortech.2008.04.004

Nikolaivits E, Dimarogona M, Fokialakis N, Topakas E (2017) Marine-derived biocatalysts: importance, accessing, and application in aromatic pollutant bioremediation. Front Microbiol. https://doi.org/10.3389/fmicb.2017.00265

Niti C, Sunita S, Kamlesh K, Rakesh K (2013) Bioremediation: an emerging technology for remediation of pesticides. Res J Chem Environ

Oktem YA, Ince O, Sallis P, Donnelly T, Ince BK (2008) Anaerobic treatment of a chemical synthesis-based pharmaceutical wastewater in a hybrid upflow anaerobic sludge blanket reactor. Bioresour Technol. https://doi.org/10.1016/j.biortech.2007.02.036

Owen G, Bandi M, Howell JA, Churchouse SJ (1995) Economic assessment of membrane processes for water and wastewater treatment. J Membr Sci 102:77–91

Padoley KV, Saharan VK, Mudliar SN, Pandey RA, Pandit AB (2012) Cavitationally induced biodegradability enhancement of a distillery wastewater. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2012.03.054

Pant D, Van Bogaert G, Diels L, Vanbroekhoven K (2010) A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production. Bioresour Technol. https://doi.org/10.1016/j.biortech.2009.10.017

Parthasarathy S, Mohammed RR, Fong CM, Gomes RL, Manickam S (2016) A novel hybrid approach of activated carbon and ultrasound cavitation for the intensification of palm oil mill effluent (POME) polishing. J Clean Prod. https://doi.org/10.1016/j.jclepro.2015.05.125

Paul SA, Chavan SK, Khambe SD (2012) Studies on characterization of textile industrial waste water in Solapur city. Int J Chem Sci. http://www.solapurtexmarket.in/downloads/4_1453_10.pdf

Pilon-Smits E (2005) Phytoremediation. Annu Rev Plant Biol. https://doi.org/10.1146/annurev.arplant.56.032604.144214

Raghukumar C, Rivonkar G (2001) Decolorization of molasses spent wash by the white-rot fungus Flavodon flavus, isolated from a marine habitat. Appl Microbiol Biotechnol. https://doi.org/10.1007/s002530000579

Rajkumar D, Song BJ, Kim JG (2007) Electrochemical degradation of reactive blue 19 in chloride medium for the treatment of textile dyeing wastewater with identification of intermediate compounds. Dyes Pigments. https://doi.org/10.1016/j.dyepig.2005.07.015

Ranade VV, Bhandari VM (2014) Industrial wastewater treatment, recycling and reuse. Butterworth-Heinemann, UK

Raposo F, De la Rubia MA, Fernández-Cegrí V, Borja R (2012) Anaerobic digestion of solid organic substrates in batch mode: an overview relating to methane yields and experimental procedures. Renew Sust Energ Rev. https://doi.org/10.1016/j.rser.2011.09.008

Rayu S, Karpouzas DG, Singh BK (2012) Emerging technologies in bioremediation: constraints and opportunities. Biodegradation. https://doi.org/10.1007/s10532-012-9576-3

Rockne KJ, Reddy KR (2003) Bioremediation of contaminated sites. In: *Invited* theme paper, international e-conference on modern trends in foundation engineering: geotechnical challenges and solutions. Indian Institute of Technology, Madras. https://pdfs.semanticscholar.org/e512/0034ccfda10fd75e250054ad7e046ee294a4.pdf

Salt DE, Smith RD, Raskin I (1998) Phytoremediation. Annu Rev Plant Physiol Plant Mol Biol 49:643–668

Sangave PC, Pandit AB (2004) Ultrasound pre-treatment for enhanced biodegradability of the distillery wastewater. Ultrason Sonochem. https://doi.org/10.1016/j.ultsonch.2004.01.026

Sangave PC, Gogate PR, Pandit AB (2007) Ultrasound and ozone assisted biological degradation of thermally pretreated and anaerobically pretreated distillery wastewater. Chemosphere. https://doi.org/10.1016/j.chemosphere.2006.12.052

Sankaran K, Premalatha M, Vijayasekaran M, Somasundaram VT (2014) DEPHY project: distillery wastewater treatment through anaerobic digestion and phycoremediation—A green industrial approach. Renew Sust Energ Rev. https://doi.org/10.1016/j.rser.2014.05.062

Santos CE, Fonseca A, Kumar E, Bhatnagar A, Vilar VJ, Botelho CM, Boaventura RA (2015) Performance evaluation of the main units of a refinery wastewater treatment plant–A case study. J Environ Chem Eng. https://doi.org/10.1016/j.jece.2015.07.011

Sarkar B, Chakrabarti PP, Vijaykumar A, Kale V (2006) Wastewater treatment in dairy industries—possibility of reuse. Desalination. https://doi.org/10.1016/j.desal.2005.11.015

Saroj S, Dubey S, Agarwal P, Prasad R, Singh RP (2015) Evaluation of the efficacy of a fungal consortium for degradation of azo dyes and simulated textile dye effluents. Sustainable Water Res Manag. https://doi.org/10.1007/s40899-015-0027-2

Schnoor JL, Light LA, McCutcheon SC, Wolfe NL, Carreia LH (1995) Phytoremediation of organic and nutrient contaminants. Environ Sci Technol. https://doi.org/10.1021/es00007a002

Schrank SG, Jose HJ, Moreira RF, Schröder HF (2004) Elucidation of the behavior of tannery wastewater under advanced oxidation conditions. Chemosphere. https://doi.org/10.1016/j.chemosphere.2004.04.012

Secula MS, Cagnon B, de Oliveira TF, Chedeville O, Fauduet H (2012) Removal of acid dye from aqueous solutions by electrocoagulation/GAC adsorption coupling: kinetics and electrical operating costs. J Taiwan Inst Chem Eng. https://doi.org/10.1016/j.jtice.2012.03.003

Shanahan P (2004) Bioremediation. Waste containment and remediation technology, Cambridge, MA, Spring, Massachusetts Institute of Technology

Siles JA, García-García I, Martín A, Martín MA (2011) Integrated ozonation and biomethanization treatments of vinasse derived from ethanol manufacturing. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2011.01.096

Singh PN, Robinson T, Singh D (2004) Treatment of industrial effluents—distillery effluent. Bioresour Technol 2004:135–141

Singhal A, Thakur IS (2009) Decolourization and detoxification of pulp and paper mill effluent by *Emericella nidulans var. nidulans*. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2009.06.041

Sivaperumal P, Kamala K, Rajaram R (2017) Bioremediation of industrial waste through enzyme producing marine microorganisms. In: Advances in food and nutrition research. Academic Press. https://doi.org/10.1016/bs.afnr.2016.10.006

Slavov AK (2017) General characteristics and treatment possibilities of dairy wastewater–A review. Food Technol Biotechnol. https://doi.org/10.17113/ftb.55.01.17.4520

Snyder SA, Adham S, Redding AM, Cannon FS, DeCarolis J, Oppenheimer J, Wert EC, Yoon Y (2007) Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. Desalination. https://doi.org/10.1016/j.desal.2005.12.052

Soloman PA, Basha CA, Velan M, Balasubramanian N, Marimuthu P (2009) Augmentation of biodegradability of pulp and paper industry wastewater by electrochemical pre-treatment and optimization by RSM. Sep Purif Technol. https://doi.org/10.1016/j.seppur.2009.07.002

Sponza DT, Çelebi H (2012) Removal of oxytetracycline (OTC) in a synthetic pharmaceutical wastewater by sequential anaerobic multichamber bed reactor (AMCBR)/completely stirred tank reactor (CSTR) system: biodegradation and inhibition kinetics. J Chem Technol Biotechnol. https://doi.org/10.1002/jctb.3706

Suganthi V, Mahalakshmi M, Balasubramanian N (2013) Development of hybrid membrane bioreactor for tannery effluent treatment. Desalination 309:231–236

Svensson E, Berntsson T (2014) The effect of long lead times for planning of energy efficiency and biorefinery technologies at a pulp mill. Renew Energy. https://doi.org/10.1016/j.renene.2012.04.029

Tiku DK, Kumar A, Chaturvedi R, Makhijani SD, Manoharan A, Kumar R (2010) Holistic bioremediation of pulp mill effluents using autochthonous bacteria. Int Biodeterior Biodegradation. https://doi.org/10.1016/j.ibiod.2010.01.001

U.S. EPA. Phytoremediation Resource Guide. EPA/542/B99/ 003 (1999). Available online at http://www.epa.gov/tio

Urase T, Kagawa C, Kikuta T (2005) Factors affecting removal of pharmaceutical substances and estrogens in membrane separation bioreactors. Desalination. https://doi.org/10.1016/j.desal.2004.11.031

Vahabzadeh F, Mehranian M, Saatari AR (2004) Color removal ability of Phanerochaete chrysosporium in relation to lignin peroxidase and manganese peroxidase produced in molasses wastewater. World J Microbiol Biotechnol. https://doi.org/10.1007/s11274-004-9005-9

Vidali M (2011) Bioremediation. In: An overview. Pure and applied chemistry. https://doi.org/10.1351/pac200Juwarkar

Virkutyte J (2017) Aerobic treatment of effluents from pulp and paper industries. In: Current developments in biotechnology and bioengineering. Elsevier. https://doi.org/10.1016/B978-0-444-63665-2.00004-7

Vlyssides AG, Tsimas ES, Barampouti EM, Mai ST (2012) Anaerobic digestion of cheese dairy wastewater following chemical oxidation. Biosyst Eng. https://doi.org/10.1016/j.biosystemseng.2012.09.001

Wang JP, Chen YZ, Wang Y, Yuan SJ, Yu HQ (2011) Optimization of the coagulation-flocculation process for pulp mill wastewater treatment using a combination of uniform design and response surface methodology. Water Res. https://doi.org/10.1016/j.watres.2011.08.023

Watkinson AJ, Murby EJ, Costanzo SD (2007) Removal of antibiotics in conventional and advanced wastewater treatment: implications for environmental discharge and wastewater recycling. Water Res. https://doi.org/10.1016/j.watres.2007.04.005

Wei MC, Wang KS, Huang CL, Chiang CW, Chang TJ, Lee SS, Chang SH (2012) Improvement of textile dye removal by electrocoagulation with low-cost steel wool cathode reactor. Chem Eng J. https://doi.org/10.1016/j.cej.2012.03.086

Welander T, Löfgvist A, Selmer A (1997) Upgrading aerated lagoons at pulp and paper mills. Water Sci Technol. https://doi.org/10.1016/S0273-1223(96)00922-5

Wu TY, Mohammad AW, Jahim JM, Anuar N (2010) Pollution control technologies for the treatment of palm oil mill effluent (POME) through end-of-pipe processes. J Environ Manag. https://doi.org/10.1016/j.jenvman.2010.02.008

Yang CL, McGarrahan J (2005) Electrochemical coagulation for textile effluent decolorization. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2005.05.050

Yeap KL, Teng TT, Poh BT, Morad N, Lee KE (2014) Preparation and characterization of coagulation/flocculation behavior of a novel inorganic–organic hybrid polymer for reactive and disperse dyes removal. Chem Eng J. https://doi.org/10.1016/j.cej.2014.01.004

Yildiz YŞ (2008) Optimization of Bomaplex red CR-L dye removal from aqueous solution by electrocoagulation using aluminum electrodes. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2007.08.034

Yonar T, Sivrioğlu Ö, Özengin N (2018) Physico-chemical treatment of dairy industry wastewaters: a review. In: Technological approaches for novel applications in dairy processing. https://doi.org/10.5772/intechopen.77110

Zheng X, Shen ZP, Shi L, Cheng R, Yuan DH (2017) Photocatalytic membrane reactors (PMRs) in water treatment: configurations and influencing factors. Catalysts. https://doi.org/10.3390/catal7080224

8 Treatment Options for Acid Mine Drainage: Remedial Achievements Through Microbial-Mediated Processes

Abhishek Gupta and Pinaki Sar

Abstract

Acid mine drainage (AMD) is considered to be one of the major environmental problems faced by the mining industries due to its toxic and lethal impact on the ecosystem. Generation of million tons of mine wastes like tailings, slags, waste rocks/ore bodies, etc. are the major sources of AMD generation in metalliferous/coal mine, due to the biologically mediated oxidation of sulfidic waste. Low pH and high heavy metal and sulfate concentration are the major characteristic features of the AMD environment and considered to be lethal than single-factor pollutants. Owing to its toxic effects, development of both preventive and treatment options remain the main focus of scientific research for decades. Prevention is a better option than complex treatment processes; however, due to several environmental factors preventive measures are limited from its application in several mining locations. In order to minimize the impact of AMD on ecosystem, several remediation technologies have been developed including chemical and biological treatment options. Due to the high capital investment and other reasons, chemical technologies are less preferred over biological treatments. Nowadays, several studies have been conducted to develop promising biological treatment system to attenuate AMD and recover metals from such environment. The present chapter discusses the cause and generation of AMD, available prevention measures, and treatment technologies using metabolic capacities of sulfate-reducing bacteria (SRB), which is the main player of biological treatment system.

A. Gupta · P. Sar (✉)
Environmental Microbiology and Genomics Laboratory, Department of Biotechnology,
Indian Institute of Technology Kharagpur, Kharagpur, West Bengal, India
e-mail: psar@bt.iitkgp.ac.in

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_8

Keywords
Acid mine drainage · Bioremediation · Biostimulation · Bioaugmentation · Sulfidogenesis · Passive and active treatments · Sulfate-reducing bacteria

8.1 Introduction

Generation of million tons of waste in metalliferous/coal mines containing sulfidic minerals is a major environmental and economic concern worldwide (Nordstrom 2000; Baker and Banfield 2003). These sulfidic minerals upon oxidation generate highly acidic, metal- and sulfate-rich mine waters known as acid mine drainage (AMD) (Nordstrom 2000). AMD is considered to be a multifactor pollutant, detrimental for the receiving ecosystems including aquatic and terrestrial (Gray 1997). Numerous studies have reported the lethal impact of AMD on the aquatic life-forms (Soucek et al. 2000; Schmidt et al. 2002; Gerhardt et al. 2004; Martin and Goldblatt 2007; Van Damme et al. 2008; Gray and Delaney 2008; Jennings et al. 2008; Hogsden and Harding 2011). Owing to its extreme and toxic nature, AMD degrades the quality of river, lakes, and groundwater and also affects the terrestrial ecosystem (Nieto et al. 2007; Olıas et al. 2004; Alhamed and Wohnlich 2014; Gupta and Nikhil 2016; Roychowdhury et al. 2017; Grande et al. 2018). Both active and abandoned mines generate millions of cubic tons of AMD worldwide. In the reports from the US Forest Service 2005, 55700 mines are abandoned in the USA. Almost 15,000–23,000 km AMD-impacted streams are present across the USA (Roychowdhury et al. 2019 and references therein). Near about 600 coal mines in the Zipaquirá Mining District of Colombia generate 70,400 m^3 of contaminated mine water each month (Fenalcarbón 2006). Pérez-Ostalé et al. (2013) determined the mining-affected area in the Iberian Pyrite Belt (TPB) region and found that more than 4800 ha areas of 88 sulfidic mines were occupied by mine waste, open pit, tailing dams, etc. Recently, Grande et al. (2018) mapped the impact of AMD on the river network of the IPB. They also demonstrated that 23 water reservoirs near the IPB are also affected by AMD and have excess mining leachates than the established range by Directive 98/83/CE (regulation for the quality of the drinking water in Europe). In the preliminary evaluation of AMD in the Minas Gerias State of Brazil, it was identified that four mining sites can generate about billions of m^3 of water at pH 2–3 (de Mello et al. 2006). China has more than 63,433 metal and nonmetal mines, but the quantity of nonmetal mines surpasses 56,000 including 15,000 coal mines (Liu et al. 2018b and references therein). Shu (2003) reported the generation of 25,000 tons of waste rocks and 30,000 tons of tailings annually from the Lechang Pb/Zn mine, China. Saha and Sinha (2018) reported that more than billion tons of waste rocks and tailings are present in the mining area of Canada and have the potential to generate AMD. In India, problem of AMD is also associated with metal and coal mining areas (Tiwary 2001; Pandey et al. 2007; Equeenuddin et al. 2010; Sahoo et al. 2012). Problem of mine drainage is also present in South African mining areas (Manders et al. 2009; Ochieng et al. 2010; McCarthy 2011).

Groundwater near the mining area of Johannesburg was contaminated with AMD (Naicker et al. 2003). Chon and Hwang (2000) reported that 41 coal mines in Korea discharge about 141,000 m^3/day AMD waste.

In order to reduce the AMD impact on the ecosystem, different prevention measures have been recommended. However, owing to the various environmental factors associated with the mine environment, capital cost, and sustainability factor, application of these preventive methods to combat AMDs is restricted to only few mines/affected areas (Sahoo et al. 2013). Several remediation technologies including chemical and biological options are used to treat AMD and AMD-impacted sites (Johnson and Hallberg 2005a; Neculita et al. 2007; Skousen et al. 2017). In comparison to chemical treatments, biological treatments are preferred as they are eco-friendly, cost-effective, and sustainable in nature (Kieu et al. 2011; Hao et al. 2014). Sulfidogenic activity of the sulfate-reducing bacteria (SRB) is the prime principle of the biological treatments. In order to enhance the growth and activities of SRB, several organic carbon sources were tested, which in turn increase the alkalinity and metal precipitation process during the biological treatment of AMD. Nowadays, acidophilic/neutrophilic SRB consortium/mixture is also applied to enhance the treatment of AMD in sulfidogenic bioreactors (Nancucheo et al. 2017).

The present review chapter provides a broad account of the occurrence of AMD, its ecological impact on ecosystem, and available prevention measures and highlights the remediation options. Bioremediation-based options utilizing the SRB are described in detail including their taxonomic identity, metabolic capabilities, and processes.

8.2 Formation of Acid Mine Drainage

Exposure of sulfidic minerals/ores to air and water during mining activity generates highly acidic, metal- and sulfate-rich acid mine drainage (AMD) in the mining area (Nordstrom 2000). The process of AMD generation starts with the oxidation of sulfidic ores (pyrite) in presence of water and air resulting in the formation of Fe^{2+}, SO_4^{2-}, and H^+ (Eq. 8.1).

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \tag{8.1}$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \tag{8.2}$$

The ferrous ions further oxidize to ferric ions (Fe^{3+}), which act as an oxidizing agent for sulfidic ores (Eqs. 8.2 and 8.3) and also form ferric hydroxide as iron precipitates (Eq. 8.4).

$$2FeS_2 + 14Fe^{3+} + 8H_2O - \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{8.3}$$

$$4Fe^{3+} + 12H_2O \rightarrow 4Fe(OH)_3 + 12H^+ \tag{8.4}$$

The generation of H^+ ion increases acidity by reducing the pH of mine drainage which leads to the dissolution of other toxic heavy metals such as cadmium, copper, zinc, cobalt, nickel, lead, chromium, etc. from the host rocks or ores. These toxic metals are highly soluble in acidic environment, hence making the mine drainage hazardous to the environment (Nordstrom and Alpers 1999; Nordstrom 2000). At low pH (3–4), the oxidation of sulfidic ores is very slow (Diaby et al. 2007), but the presence of highly acidophilic chemolithothrophic iron and sulfur oxidizers in mine environment makes this process feasible, as these organisms are capable of oxidizing Fe/S for their energy-generation process (Baker and Banfield 2003). It was observed that the rate of Fe^{2+} oxidation is enhanced to several folds by these iron- and sulfur-oxidizing bacteria/archaea (Diaby et al. 2007 and references therein). These microorganisms use the sulfur and iron as electron donors for their energy generation (Baker and Banfield 2003; Mendez-Garcia et al. 2015) which leads to further decrease in pH of the mine drainage. *Acidithiobacillus*, *Ferrithrix*, *Leptospirillum*, *Ferrovum*, *Picrophilus*, *Sulfobacillus*, *Ferroplasma*, etc. are the typical iron and sulfur oxidizers involved in acid mine generation (Mendez-Garcia et al. 2015; Chen et al. 2016; Teng et al. 2017).

8.3 Ecological Impact of Acid Mine Drainage

Acid mine drainage is a multifactor system which causes ecological instability due to its hazardous nature. The major factors such as acidity and metal and sulfate concentrations vary and depend upon the prevailing geochemistry of the environment. These factors make the life of both terrestrial and aquatic systems unsustainable (Fig. 8.1). It affects the food chain, increases loss of species, changes the

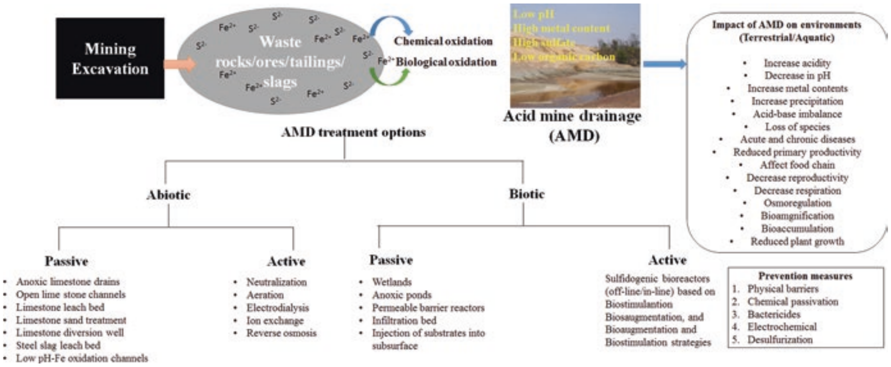


Fig. 8.1 Overview of AMD generation and its impact on environment, prevention options, and remediation strategies

community structure of ecosystem, increases acidity/metal precipitation/soluble metal concentration, and reduces pH (Gray 1997). These deleterious effects of AMD on ecosystem are more pronounced than single-factor pollutants and can be divided into four different categories (chemical, physical, biological, and ecological) (Gray 1997).

High concentration of heavy metals in AMD acts as a metabolic poison for the life in both terrestrial and aquatic systems. These metals when mixed with river streams, ponds, lakes, etc. produce hydroxide precipitate, which in turn reduces the oxygen content for life and also covers the body surface of several organisms and bed of these water bodies, hence making the life of both pelagic and benthic population inhabitable (Soucek et al. 2000; Schmidt et al. 2002; Gerhardt et al. 2004; Jennings et al. 2008; Qiu et al. 2009; Casiot et al. 2009; Hogsden and Harding 2011). Brown and Sadler (1989) reported that the loss of sodium ions from blood and oxygen in the tissue due to the accumulation of precipitates of heavy metals in gills (affect the breathing) was the main cause of fish death in AMD-contaminated water bodies. It has been found that streams that have normal pH levels but high iron concentrations have a small fish population (Koryak et al. 1972). Slaninova et al. (2014) also reported the loss of fish due to the inflow of acidic water which contained higher amount of Al and Fe into the rearing pond. The presence of heavy metals in high amount reduces the reproduction capabilities of organisms (Walton et al. 1982; Marsden and DeWreede 2000). When AMD runoff passes through the field, it reduces pH (increase in acidity) and increases heavy metal and sulfate contents of the soil, which change the nature of the soil (Gray 1997). Heavy metals have negative influences on soil fertility by diminishing the population of soil microbiota and other decomposers of soil organic matter, hence acting as a serious threat to plant productivity (Leita et al. 1995; Giller et al. 1998). Heavy metals as micronutrient support the metabolic precursor for many enzymatic reactions in plant metabolism, but when it exceeds the permissible limit, it starts hampering the growth, reproduction, flowering, etc. (Chibuike and Obiora 2014; Shahid et al. 2015). Plants have several mechanisms to overcome the stress of heavy metals, and one of them is phytoaccumulation, which leads to the bioaccumulation of these metals in the food chain/web and hence alters the ecosystem (Chibuike and Obiora 2014). Near to the mining regions, farmers use AMD-infested water for irrigation purpose, which severely affects the fertility of field (due to the acidity of AMD and accumulation of excessive heavy metal contents) and crop productivity (Garrido et al. 2009; Sun et al. 2015; Liao et al. 2016). Humans also have an indirect effect of AMD on their life. AMD-affected water bodies have low pH and high toxic metal concentration, which are used by the local population for their day-to-day life (He et al. 2018). These toxic metals cause serious diseases related to liver, kidney, brain, reproduction, etc. in humans (Jaishankar et al. 2014). It is of utmost importance to develop proper remediation technologies that can reduce its hazardous impacts on the ecosystem and continue with mining in more sustainable ways.

8.4 Acid Mine Drainage (AMD) Prevention and Control Options

Control and prevention options are considered to be of great importance to eliminate the sulfur oxidation event in waste rock and tailings, thus reducing AMD generation. There are several ways through which this can be achieved, but this is not feasible in many mining sites due to short life span or cost-intensiveness (Sahoo et al. 2013 and references therein). Five different prevention options are available: (i) physical barriers, (ii) bacterial inhibition (bactericides), (iii) chemical passivation, (iv), electrochemical, and (v) desulfurization (Kuyucak 2002) (Fig. 8.1). **Physical barriers** include dry and wet covers which are used to prevent the oxidation of pyritic minerals. Soil covers, plastic liners, and organic wastes have been used as dry covers to limit the oxygen transfer and oxidation of sulfidic minerals in mining region (Backes et al. 1987; Yanful and Payant 1992; Yanful and Orlandea 2000; Timms and Bennett 2000; Kuyucak 2002; Pandey et al. 2011). Water covers have also been used to prevent the oxidation of sulfidic minerals due to two reasons (i) low solubility of oxygen and (ii) diffusion rate in water as compared to air (Kuyucak 2002; Demers et al. 2008). Prevention of water migration from mining wastes via constructing interceptor structures, slurry walls, and diversion ditches also play an important role in limiting AMD generation (Kuyucak 2002). Vegetative covers are also reported as an option for reducing the acid generation, as well as phytostabilization potential of plants for accumulation of heavy metals (Reid and Naeth 2005; Tamas and Kovacs 2005; Valente et al. 2012; Wang et al. 2017). **Bactericidal** effect on mine tailings also provides a limited time span prevention option by killing the iron- and sulfur-oxidizing bacteria responsible for AMD generation (Kuyucak 2002; Sahoo et al. 2013 and references therein). Anion surfactants such as sodium dodecyl sulfate (SDS), sodium lauryl sulfate (SLS), and organic acids were found to be effective in reducing the growth and activity of iron- and sulfur-oxidizing bacteria (Kuyucak 2002; Lottermoser 2007). Benzoic acids, fatty acids, amines, etc. were tested at lab scales and were found to be effective in limiting the pyrite oxidation (Kleinmann et al. 1981; Onysko et al. 1984). **Chemical passivation** is another technique for AMD prevention which deals with the use of chemically inert organic and inorganic materials for coating the surface of sulfidic minerals to limit its oxidation (Zhang and Evangelou 1998). Various organic (humic acid, lipids, fatty acids, polyethylene polyamine, alkoxysilanes, oxalic acid, catechol, 1, 3-benzenediamidoethanthiol, etc.) and inorganic (phosphate, silica, permanganate, alkaline materials, etc.) coating materials are used nowadays to prevent AMD generation from sulfidic minerals (Elsetinow et al. 2003; Zhang et al. 2003a, b; Khummalai and Boonamnuayvitaya 2005; Hao et al. 2009; Ačai et al. 2009; Liu et al. 2013; Shu et al. 2013; Park et al. 2018). Huang and Evangelou (1994) introduced a new microencapsulation technique that uses soluble phosphate salt, hydrogen peroxide, and sodium acetate to form a stable ferric phosphate coating on iron sulfide minerals, which inhibits its oxidation by limiting the oxidant. **Electrochemical** is a process in which sulfidic minerals act as an electrode as these minerals are known to behave like electronic conductors (Shelp et al. 1995). Several laboratory and field tests were conducted by

ENPAR Technology Inc. 2000 and Shelp et al. (1995) where sulfide tailings were converted into electrodes of an electrochemical cell which removed the dissolved oxygen and lowered the redox potential, forming a thermodynamically stable environment and eventually inhibiting the pyrite oxidation. ENPAR Technology Inc. installed a pilot-scale electrochemical system on the pyrrhotite tailings in the Sudbury basin (Ontario, Canada) and Golden Sunlight Mine tailings of Montana, USA, in 2000 and 2002, respectively. **Desulfurization** is a method based on froth flotation principle which is widely used these days to separate sulfide-rich minerals from the waste, resulting in low-sulfur containing tailings which are non-acid generating (Benzaazoua et al. 2000; Hesketh et al. 2010; Nagase et al. 2011).

8.5 Acid Mine Drainage Treatment Options

In order to minimize the impact of AMD on the receiving environments such as rivers, soil, and groundwater, two major types of treatment options are available: (i) abiotic treatment (application of neutralizing agents to neutralize the AMD with precipitation of metals) and (ii) biotic treatment (application of biostimulation and bioaugmentation agents). Both abiotic and biotic remediation strategies are divided into two parts: (i) active and (ii) passive (Fig. 8.1).

8.5.1 Abiotic Remediation Strategies

8.5.1.1 Active Technologies

A wide range of neutralization materials is available that can be used for the treatment of AMD (Johnson and Hallberg 2005a; Skousen et al. 2017). These neutralization agents (limestone, quicklime, hydrated lime, magnesite, dolomite, ammonia, sodium hydroxide, cement kiln dust, barium hydroxide, barium carbonate, fly ash, lime kiln dust, etc.) increase the pH of the AMD which lead to the precipitation of certain heavy metals. This pH-dependent metal precipitation is applicable for most of the heavy metals (Cu, Ni, Zn, Fe, Ag, Se, Pb, Cd, Th, Be, and Sb) but few remain unaffected [Hg. Cr (VI), Mo, and As (III)] or uncertain (Co and Bi) [Taylor et al. 2005]. This neutralization technology is adopted by several mines worldwide to reduce the acidity and recover the metals from the AMD (Skousen et al. 2017 and references therein). The choice of the neutralization agent depends upon the mine type or the metal contents of the AMD (Trumm 2010). Each neutralization agent has specific chemical properties like solubility and pH (Taylor et al. 2005). Calcium- and magnesium-based carbonate materials can be used as neutralization agents for this application but few carbonate minerals such as siderite, rhodochrosite, and ankerite may increase the acidity of Fe and Mn upon treatment of AMD (Taylor et al. 2005). There are other important active treatment options available including reverse osmosis, aeration, ion exchange, electrodialysis, and natural zeolites (Feng et al. 2000; Potgieter-Vermaak et al. 2006; Zhong et al. 2007; Motsi et al. 2009; Buzzi et al. 2013; Rodríguez-Galán et al. 2019 and references therein). Active treatments are useful in minimizing the detrimental effect of AMD, but it has few disadvantages like (i) it requires continuous input of chemicals, (ii) it is expensive, (iii) some of the chemicals are toxic and require safe handling, and (iv) it is labor- intensive.

8.5.1.2 Passive Technology

Abiotic passive treatment of AMD includes anoxic limestone drains (ALD), open limestone channels (OLC), limestone leach bed (LLB), limestone sand treatment (LST), steel slag leach bed (SSLB), limestone diversion well (LDW), and low-pH Fe oxidation channels (Skousen et al. 2017). These strategies are economically more cheap and eco-friendly than active treatment. **Anoxic limestone drain** (ALD) is the approach where limestone drain is covered to avoid the passage of air into the drain system, and to keep the dissolved iron in the reduced form (Skousen et al. 2017 and references therein). This process is applicable if the dissolved oxygen concentration is below 1mg/L (Taylor et al. 2005). In this system limestone dissolves and increases the pH by adding bicarbonate alkalinity (Taylor et al. 2005). Long residence time is encouraged for higher efficiency as well as low DO is required; otherwise armoring of the limestone takes place with iron minerals, reducing the rate of limestone dissolution. **Open limestone channel** (OLC) is the drainage system equipped with large coarse limestone over which AMD flows (Skousen et al. 2017). There are several studies in which the efficiency of OLCs has been assessed for the treatment of AMD (Ziemkiewicz et al. 1997; Ziemkiewicz and Brant 1996; Cravotta 2007; Cravotta III 2008a, b; Cravotta and Ward 2008). These studies reported the higher neutralization efficiency of the incoming AMD. It requires a large area for effective operation and gradient of the slope of the drainage such that it neither passes the AMD very quickly nor accumulates the metal precipitates within the void spaces (Skousen et al. 2017). **Limestone diversion well** (LDW) is consisted of well with crushed limestone. The AMD stream is diverted into these wells through pipelines to increase the alkalinity of the AMD and reduce the acidity with metal precipitation. Armoring of limestone is less due to the adequate mixing of water. Reduction of acidity with increase in pH was observed in a few studies using LDW for treatment of AMD (Arnold 1991; Faulkner and Skousen 1994; Ziemkiewicz and Brant 1996). **Limestone leach bed** (LLB) is a small basin carrying small-sized limestones to treat AMD or mine discharge. It can be constructed near an AMD seep or underground mine drainage (Skousen et al. 2017 and references therein). A minimum of 30 min time is sufficient to reduce 50% acidic load of moderately acidic AMD (Black et al. 1999). It was suggested that LLB was useful at the upstream of OLC, as it shortened the time and improved the efficiency (Ziemkiewicz et al. 2003). A manually flushed upflow LLB was constructed at Strattanville, PA, to treat water with 400– 650 mg L^{-1} acidity and pH 4.5 at a flow rate of 380–570 L min^{-1} (Schueck et al. 2004). **Limestone sand treatment** (LST) can be used for treatment of AMD stream by the addition of sand-size limestone to the stream (Skousen et al. 2017). It causes precipitation of heavy metals due to neutralization of AMD, and armoring of limestone is less due to agitation caused by the flowing streams. **Steel slag leach beds** (SSLB) are used to treat AMD due to the alkalinity content (45–78% $CaCO_3$) of basic steel slag. Slags generated from stainless steel are toxic than basic steel slags. So it can be used as a potent neutralization agent for AMD treatment. AMD and metal-free water with acidity were treated by slag (Ziemkiewicz and Skousen 1998; Simmons et al. 2002a, b; Skousen et al. 2017 and references therein). **Low-pH Fe oxidation channels** can be used to partially treat high Fe discharges (Skousen et al. 2017). In this technique, a shallow channel is built lined with limestone or sandstone to increase the Fe oxidation.

8.5.2 Biological Remediation Technologies

The capacity of iron- and sulfate-reducing microorganisms plays substantial roles in generating alkalinity, heavy metal removal, sulfate reduction, and metal recovery, thereby attenuating the AMD-generation process (Johnson and Hallberg 2005a; Roychowdhury et al. 2015). Macrophytes are also known to play an important role in metal removal in various wetland systems (Roychowdhury et al. 2015). The excessive presence of Fe^{3+} and SO_4^{2-} in the AMD system tends to be of major importance as they can generate alkalinity with the help of their respective reducing microbial populations. AMD system is very low in organic carbon content (less than 10 mg/L), as a result of which these indigenous microorganisms cannot promote iron- and sulfate-reducing events naturally (Johnson 2012). In order to promote the growth and activities of these microorganisms, supplementation of organic carbon substrates is required. These organic carbons act as electron donors while the available Fe^{3+} and SO_4^{2-} act as electron acceptors for these microbial populations. Sulfate-reducing members on undergoing dissimilatory sulfate reduction process generate H_2S which increases the pH of the system. On the contrary, iron reduction by iron-reducing populations generates Fe^{2+} in the system which on reaction with H_2S forms iron sulfide, thereby removing the iron and sulfate contents from the AMD system with raise in pH (Fig. 8.2). Other metals present in the AMD such as Cu, Ni, Zn, and Cd also get precipitated in the form of their metal sulfides upon reaction with H_2S. Biologically mediated remediation technologies are presented in this section in details.

8.5.2.1 Passive Treatment Options

Different passive biological treatment options are available which can be used for the development of environment-friendly and sustainable technology for remediation of AMD (Johnson and Hallberg 2005a). **Wetland** systems (aerobic and anaerobic) have been employed to eliminate metals and sulfate and reduce the acidity of AMD by chemical, physical, microbial, and plant-mediated processes (Pat-Espadas et al. 2018). Aerobic wetlands depend upon the oxidation of metals and precipitation of metals in the form of metal hydroxides (Roychowdhury et al. 2015). Wetland plants remove the metals from the AMD via rhizofiltration (adsorption/adsorption/precipitation of metals in rhizosphere) and phytoextraction (uptake of metals and store them in plant bodies) (Roychowdhury et al. 2015 and references therein). Anaerobic wetland system utilizes the potential of SRB for removal of heavy metal via metal precipitation through sulfate reduction (Pat-Espadas et al. 2018). There

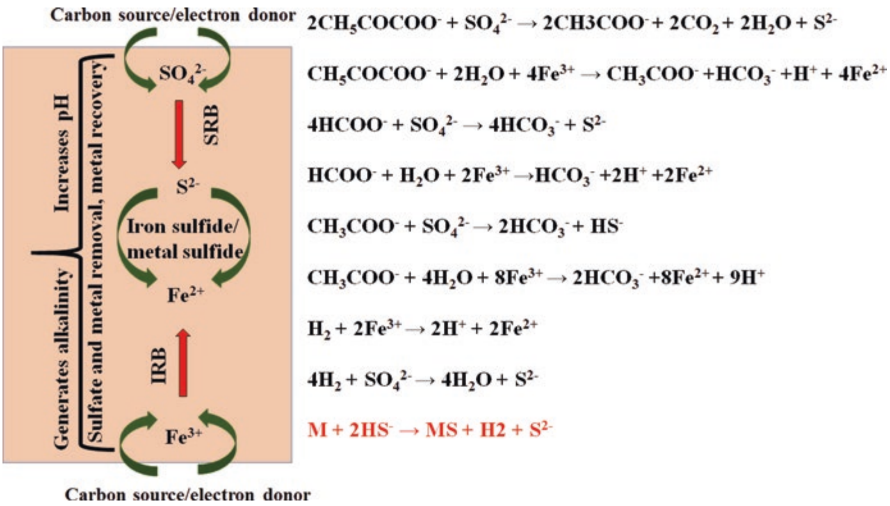


Fig. 8.2 Mechanism of sulfate- and iron-reducing bacteria in bioremediation of AMD. SRB and IRB indicate sulfate- and iron-reducing bacteria. Biochemical reactions operated by SRB/IRB during sulfate/iron reduction processes while using organic carbons (lactate, formate, and acetate) and H_2. Metal precipitation reaction is represented in red (M: Metal)

are reports where constructed wetland systems decreased the heavy metal contents up to a great extent and reduced the acidity of AMD (Sheoran and Sheoran 2006; Nyquist and Greger 2009; Sheoran 2017; Pat-Espadas et al. 2018). Acidity of AMD, metal contents, and seasonal variations are considered to be important factors of wetland system to enhance the performance of AMD treatment. **Permeable reactive barrier (PRB)** is the treatment option for AMD where a reactive barrier is installed in the path of contaminated water flow (Benner et al. 1999). Reactive mixture includes limestone and organic matter which promote the activities of SRB, leading to the decrease in metal and sulfate contents and acidity (Benner et al. 1997; Waybrant et al. 1998)). The potential of different organic matters for reactive mixture had been tested for treatment of AMD, and many other studies have been conducted to assess the potential of PRB in remediation (Blowes et al. 2000; Gibert et al. 2004; Golab et al. 2006; Pagnanelli et al. 2009; Gibert et al. 2011; Shabalala et al. 2014 and references therein). **Infiltration bed** technology passes the surface water contaminated with AMD from the channel comprising a bed of organic substrates that promote and sustain the SRB activities (Vestola 2004). This study reported the removal of Cu, Zn, Fe, and Mn from the AMD-contaminated water up to 99%. **Anoxic pond** is the open pit which receives AMD and treatment of AMD is performed via addition of organic substrates and SRB (Riekkola-Vanhanen and Mustikkamaki 1997). It was reported that increase in sulfate-reduction activity was observed during treatment of AMD in anoxic pond upon supplementation with liquid manure and press juice from silage. Increase in SRB activities resulted in the decrement of heavy metal and sulfate concentration with slow rise in pH (Riekkola-Vanhanen and Mustikkamaki 1997). **Injection of substrates into subsurface** is the method to treat the groundwater contaminated by AMD by enhancing the growth and activity of SRB through injecting the substrates into the subsurface by boreholes (Canty 1999). Canty (1999) reported the increase in pH and removal of Al, Cd, and Zn from mine wastewater flowing through the mine shaft containing organic substrates. Unwanted discharge of substrates, leakage, and spill outs are the major concerns of this method (Canty 1999).

8.5.2.2 Active Treatment Options

Active treatment options of biologically mediated remediation technology depend upon the sulfidogenic activity of the sulfate-reducing microorganism. The sulfidogenic activity of the microorganisms radically improves the process of remediation to mitigate the impact of AMD on ecosystem. There are several advantages of active biological treatment systems such as recovery of selective heavy metals, lowering of significant amount of sulfate and heavy metals from the AMD, along with predictable and readily controllable performance of the treatment system (Jonhson and Hallberg 2005a, b; Neculita et al. 2007; Kefeni et al. 2017; Nancucheo et al. 2017; Kiran et al. 2017). Due to these properties, this technology is preferred over the passive treatment options. There are several reports in the literature where sulfidogenic bioreactors were used to treat AMD or wastewater containing heavy metals through sulfate reduction process (Hao et al. 2014; Kefeni et al. 2017; Nancucheo et al. 2017 and references therein). In the current scenario, in order to remediate AMD/acidic mine water, researchers have been employing neutrophilic sulfate-reducing populations in offline bioreactor system, i.e., avoiding the direct exposure of SRB to the acidic water which are lethal to them (Nancucheo et al. 2017). In contrast, few studies have been conducted to treat AMD with the help of acidophilic SRB in sulfidogenic bioreactors (Kimura et al. 2006; Nancucheo and Johnson 2012, Hedrich and Johnson 2014; Santos and Johnson 2017; Johnson and Santos 2018; González et al. 2019).

Several studies have been conducted using the different kinds of sulfidogenic bioreactors/microcosms/mesocosms for the treatment of acid mine drainage which include either of the strategies: (i) biostimulation, (ii) bioaugmentation, and (iii) biostimulation and bioaugmentation (Jong and Parry 2003; Kaksonen et al. 2004; Church et al. 2007; Neculita et al. 2007; Hiibel et al. 2008; Becerra et al. 2009; Bijmans et al. 2009; Hiibel et al. 2011; Neculita et al. 2011; Burns et al. 2012; Nancucheo and Johnson 2012; Xingyu et al. 2013; Zhang and Wang 2016; Nancucheo and Johnson 2014; Lefticariu et al. 2015; Zhang et al. 2016; Kefeni et al. 2017; Vasquez et al. 2018; Johnson and Santos 2018; González et al. 2019). Biostimulation and bioaugmentation are complementing each other as these strategies provide substantial remediation efficiencies than any other systems (Tyagi et al. 2011). Biostimulation denotes the addition of organic carbon as electron donor or nutrient in nutrient-deficient systems to enrich the indigenous population for the remediation purpose. Bioaugmentation describes the addition of extraneous culture of single isolates capable of performing desired functions. Biostimulation and bioaugmentation approaches denote the supplementation of nutrient and biological culture/strain in the treatment systems.

8.5.2.2.1 Biostimulation-Based Bioremediation of AMD or Mine Discharge

Different biostimulation agents were used to promote the growth and activities of SRB for the treatment of AMD. Table 8.1 tabulates the amendment use for the biostimulation-based bioremediation of AMD. A detailed list of biostimulation studies performed in last 15 years was prepared and tabulated with their major findings and type of amendments used for achieving the bioremediation goals (Table 8.1). In this section, only those studies are described where microbiological investigation was performed through mesocosms, microcosms, and bioreactors-based treatment of AMD to understand the role of indigenous microbiota in such process (Table 8.2). Kaksonen et al. (2004) reported the use of lactate and ethanol for sulfate reduction to treat AMD and found that microbial diversity of ethanol-fed bioreactors was more diverse than lactate-fed ones and were mostly dominated by members of *Proteobacteria* (especially *Deltaproteobacteria*). Kaksonen et al. (2006) reported the use of ethanol in sulfate reduction and higher HRT promoted sulfate removal up to 81%. Members such as *Desulfovibrio*, *Desulfotomaculum*, *Desulfobulbus*, *Desulforhabdus*, and *Desulfobacca were found to be involved in sulfate reduction process in this study*. Zagury et al. (2006) attempted to remediate the AMD through addition of six different organic carbon substrates to enhance the sulfate reduction and metal precipitation in batch reactors. The results suggested enhanced metal removal efficiencies (94–99% for Zn, Ni, Cd, Mn, and Fe). This study also suggested that mixture of organic materials was found to better in terms of sulfate reduction followed by ethanol, maple woods, and single substrates. Increase in several orders of SRB cell numbers from initial day to the end of experiment suggested the role of organic carbons in enhancing the activities of SRB. Church et al. (2007) reported the sulfate reduction at low pH and confirmed the involvement of SRB members such as *Desulfosporosinus, Bacillus,* and *Clostridium* in sulfate reduction process. Hiibel et al. (2008) compared the microbial community structure of two field-scale pilot sulfate-reducing bioreactors different in configurations used for treating AMD. The results showed that around 60% sulfate were removed from the AMD in one of the reactors, which was almost 40% greater than other bioreactors. The increase in abundance of *Desulfovibrio* taxa was quantified by qPCR, and clone library suggested that the presence of SRB (*Desulfosporosinus*, *Desulfobulbus*, and *Desulfovibrio*) in the bioreactors confirmed the enhanced reduction of sulfate. The effect of three different organic substrates (ethanol, hay and wood chips, and corn stover and wood chips) on the performance and microbial communities present in pilot-scale biochemical reactors treating mine drainage were observed (Hiibel et al. 2011). Results revealed the differences in microbial diversity across the bioreactors fed with different substrates. *Desulfovibrio* and *Desulfomicrobium* were the dominant species detected in the bioreactors. Behum et al. (2011) reported successful treatment of AMD through anaerobic sulfate-reducing bioreactor with increase in pH up to 6.8, 99% removal of Fe and Al, and 42% reduction in sulfate content. *Desulfobacca* was found to be the dominant SRB in this treatment. Burns et al. 2012 demonstrated the performance of pilot-scale bioreactor and microbial community dynamics treating AMD. The results indicated the successful increase in pH from 3.09 to 6.56 with lowering of total iron and sulfate levels upto 95.9% and 67.4%,

Table 8.1 Selected AMD remediation studies conducted in last 15 years through biostimulation-based approach in bioreactors, mesocosms, and microcosms

S. no.	Materials	Amendment	Selected finding	Reference
1	Synthetic mineral processing waste water	Ethanol and lactate	Increased in pH and metal precipitation	Kaksonen et al. (2003, 2004)
2	Mine drainage waste water	Lignocellulose	Reduction in sulfate concentration and pH increment	Clarke et al. (2004)
3	Sediment and water	None	Effluent S2- > influent sulfide, effluent pH > influent pH, black precipitate	Monserrate (2004)
4	Sediment and water	Postgate B medium	pH increased to 7, sulfate reduced to 15 mM from 20 mM, ORP decreased	Harrison (2005)
5	AMD	Softwood sawdust, hay, and a small amount of cattle manure	Sulfate removal (23–62%), iron reduction, sulfide detection, and zinc removal	Johnson and Hallberg (2005b)
6	Acidic water	Calcite, municipal compost, and river sediment	Acidity neutralization due to calcite dissolution not because of bacteria activity, Co precipitation of Fe- and Al-(oxy) hydroxide	Gibert et al. (2005)
7	Synthetic AMD	15% Walnut wood shavings, 20% dairy cattle manure, 10% alfalfa pellets, 5% wetland sediment (Big Five treatment wetland, Idaho Springs, CO), 5% crushed limestone rock	Increase in pH and metal precipitation and reduction in sulfate concentration	Logan et al. (2005)
8	AMD	Leaf compost amended to 3:1 (vol:vol) with a mixture of cattle/horse manure and sewage sludge	Increase in pH and reduction in sulfate concentration	Morales et al. (2005)
9	Synthetic AMD	Various organic reactive mixtures	pH increased to 7.5–8.5 and reduction in sulfate concentration	Zagury et al. (2006)
10	Mine water	Ethanol and lactate	Sulfate removal and metal removal	Kaksonen et al. (2006)
11	Sediment and water	Municipal waste	pH changes to 3.9–4.1, sulfate and iron concentration increased	Adams et al. (2007)

(continued)

Table 8.1 (continued)

S. no.	Materials	Amendment	Selected finding	Reference
12	Sediment	Nutrient medium	Metal reduction at pH 4.0; release of H2S and metal precipitation of Cu, Cd, and Zn	Church et al. (2007)
13	Sediment and water	N+P+glycerol	pH increased to 5.0 from 2.7, black precipitate, increasing total iron concentration	Lopez-Luna (2008)
14	Pyrite powder + water	Effluent solid (wastewater treatment plant, returned milk, and lactate)	pH increased from 4.78 to circum-neutral, sulfate reduction and black precipitate was observed	Jin et al. (2008)
15	AMD	Shredded lodgepole pine woodchips (13–50 mm), 40% lodgepole pine sawdust, 29% limestone, 10% alfalfa hay, 1% kiln dust, and 10% dairy cow manure	Increase in pH and sulfate removal	Hiibel et al. (2008)
16	AMD	Maple wood chips, sawdust, leaf compost and poultry manure, sand, creek sediment, urea, and calcium carbonate	Increasing the pH and alkalinity of contaminated water and for SO4 and metal removal (60–82% for Fe and up to 99.9% for Cd, Ni and Zn)	Neculita et al. (2008)
17	Waste and process water	Formate	Sulfate reduction	Bijmans et al. (2009)
18	Sediment and water	N+P+glycerol	pH increased to 6.0 from 3.5, Fe2+ increased from 50 mg/L to200 mg/L, sulfate varied	Becerra et al. (2009)
19	Acidic wastewater	Yeast extract and lactate	Sulfate reduction and zinc removal (99%)	Bayrakdar et al. (2009)
20	Sediment	Organic carbon	Iron and sulfate reduction, pH elevated	Wendt-Potthoff et al. (2010)
21	Synthetic AMD	Reactive mixture	pH increased from 3.9–4.3 to 7.73	Neculita et al. (2010)
22	AMD	Limestone, compost, straw, woodchips, and municipal yard waste	pH increased to 6.2; reduction in sulfate, iron, and aluminum concentration were observed	Behum et al. (2011)
23	Mining-influenced water	Wood chips, limestone, horse manure (as inoculum), and hay (HYWD 3,4) or corn stover	Increase in pH and sulfate removal	Hiibel et al. (2011)

(continued)

Table 8.1 (continued)

S. no.	Materials	Amendment	Selected finding	Reference
24	AMD	Postgate B medium	pH increased to 6.5, 72% sulfate removal and >99% metals removal	Martins et al. (2011)
25	Synthetic AMD	Ethanol	Increment in pH to 7.0–8.0, 99% removal of metals except Mn	Bekmezci et al. (2011)
26	Mine pit lake	Sewage waste	Fe reduction, increase in pH to circum-neutral	McCullough and Lund (2011)
27	Sediment	Glycerol, nitrogen, and jarosite	pH increased to 5.75, reduction in sulfate was observed	Coggon et al. (2012)
28	Synthetic AMD	Domestic wastewater treatment	Sulfate (>75%), Fe (>85%), and other dissolved metals (>99% except for Mn) were achieved	Sanchez-Andrea et al. (2012)
29	Simulated mine drainage	Woody material and alfalfa as well as carboxymethyl cellulose, ethanol, and manure	Reduction in sulfate concentration	Pereyra et al. (2012)
30	AMD	Limestone and compost	pH increased to 6.55 and 67% reduction in sulfate concentration	Burns et al. (2012)
31	Artificial AMD	Mushroom compost, woodchip, saw dust	Iron and AL, removal, sulfide detection, pH increment	Song et al. (2012)
32	AMD	Activated sludge	Sulfate removal, metal removal, and precipitation	Xingyu et al. (2013)
33	As-containing simulated AMD	Ethanol	pH increased to 6–8, and 90% reduction in sulfate and 98–100% As removal	Sahinkaya et al. (2015)
34	Sediment	Different organic mixture	pH increased to 6.4, sulfide detected, sulfate reduction was observed	Lefticariu et al. (2015)
35	AMD	Wastewater and activated sludge	Sulfate removal	Deng et al. (2016)
36	AMD	Mulch and compost	Increase in pH, removal of metals and sulfate	Clyde et al. (2016)
37	AMD	Cow manure, mushroom compost, sajo sawdust, gravel, limestone, and wetland sediment as inoculum	Increase in pH and alkalinity, reducing sulfate (>70%), and removing Fe2+ and Zn2+ (>99%),	Vasquez et al. (2016a, b)

(continued)

Table 8.1 (continued)

S. no.	Materials	Amendment	Selected finding	Reference
38	Tailings	Yeast extract and tryptone	pH increased to neutral	Zhang et al. (2017)
39	AMD	Rice bran	Increase in pH and sulfate removal	Sato et al. (2018)
40	Synthetic AMD	Glycerol	Sulfate and metal removal	Santos and Johnson (2017)
41	AMD	Glycerol, NH4Cl, K2PO4, and SRB	Increase in pH, removal of As, Zn	Le pape et al. (2017)
42	Mining-influenced water	Manure, Alfalfa hay, pine woodchips, and sawdust	Zinc removal	Drennan et al. (2017)
43	AMD-impacted soil	Cysteine	pH increased to 6.37 from 3.5, 75% reduction in sulfate, increased in Fe concentration and black precipitate was observed	Gupta et al. (2018)
44	AMD-impacted soil	Cysteine +lactate	pH increased to 6.61 from 3.5, 95% reduction in sulfate, 0.6-fold decrease in Fe and black precipitate was observed	Gupta et al. (2018)
45	Synthetic AMD	Limestone (LS, 40% v/v), spent mushroom compost (SMC, 30%), activated sludge (AS, 20%), and woodchips	Sulfate removal, metal removal	Muhammad et al. (2018)
46	AMD	Baggase	Increase in pH, metal removal	Grubb et al. (2018)
47	AMD	Sediment from AMD, fresh cow manure, and domestic-activated sewage sludge	Reduction in sulfate concentration and metal removal	Giachini et al. (2018)
48	AMD	Cellulosic material	Higher sulfate reduction rates, high removal of iron	Perez et al. (2018)
49	AMD	Cow manure, mushroom compost, sajo sawdust, gravel, limestone, and wetland sediment as inoculum	Sulfate reduction	Vasquez et al. (2018)
50	AMD	Molasses	Sulfate reduction and Zn and Cd removal up to 90%	Nielsen et al. (2018)

Table 8.2 Bioaugmentation- and biostimulation-based approaches used for bioremediation of AMD

S. no.	Material	Amendment	Selected finding	Reference
1	AMD	SRB and lactate	Increase in pH and sulfate removal	Elliott et al. (1998)
2	AMD	SRB and ethanol	Sulfate reduction	Kolmert and Johnson (2001)
3	Acidic metal water	SRB and lactate	Increase in pH and sulfate and metal removal	Jong and Parry (2003)
4	Simulated AMD	SRB and manure	pH increased to 8.0, removal of metals and sulfate	Pruden et al. (2007)
5	Waste water	Sulfur- and sulfate-reducing bacteria and zerovalent iron	Hydrogen sulfide production, copper precipitation, and proton consumption	Jameson et al. (2010)
6	AMD	SRB and rice straw	Metal and sulfate removal	Lu et al. (2011)
7	AMD	SRB and glycerol	Zinc sulfide formation and sulfate removal	Nanchucheo and Johnson (2012)
9	AMD	SRB, lactate, and yeast extract	Increase in pH and sulfate removal	Bai et al. (2013)
10	AMD	SRB and glycerol	Metal precipitation up to 99% and sulfate reduction	Hedrich and Johnson (2014)
11	Synthetic AMD	Immobilized SRB with postgate C medium	pH increased to 7.8–8.0, 99% reduction in metals	Zhang and Wang (2016)
12	Synthetic AMD	Immobilized SRB with maize straw and lactate	pH increased to 7.3–7.8, 61–88% reduction in sulfate and >99% reduction in metals	Zhang et al. (2016)
13	Synthetic AMD	SRB and sewage sludge	Increase in pH and sulfate removal	Liu et al. (2018a)
14	AMD	SRB and lactate	Sulfate and zinc removal	Hwang and Jho (2018)
15	Synthetic AMD	SRB and glycerol and yeast extract	Sulfate reduction at low pH and copper removal	Johnson and Santos (2018)
16	AMD	Glycerol and yeast extract	Increase in pH and metal removal	Gonzalez et al. (2019)

respectively. The microbial diversity was assessed through 16S rRNA gene and dsrA gene-based clone library, and the results suggested the involvement of various SRB members. Nancucheo and Johnson (2012) treated synthetic AMD using glycerol and confirmed 98% reduction in sulfate with the help of sulfate-reducing bacteria (*Desulfosporosinus*). Lefticariu et al. (2015) suggested that organic carbon substrates are promising agents for the enhancement of sulfate reduction. In this study different herbaceous and woody organic substrate along with limestone amended bioreactors were used to treat AMD and the results showed the increase in herbaceous content resulted in more sulfate and metal removal. Microbial diversity analysis also confirmed the increase in cellulolytic and fermentative bacteria along with sulfate reducers. In another study, where different organic reactive mixtures were tested on the treatment of AMD along with role of different hydraulic retention times (HRT) on efficiency, reactive mixture and microbial diversity was also assessed (Vasquez et al. 2016a, b; Vasquez et al. 2018). The results from these studies suggested that mixtures were found to increase the pH and alkalinity, reduced the sulfate (>70%), and removed Fe^{2+} and Zn^{2+} (>99%). Different retention times also enhanced the pH and reduced the sulfate content, but the best was observed with 4 days HRT. The microbial diversity assessment of these bioreactors during the treatment suggested the enhancement in abundance of SRB belonging to genera *Desulfovibrio, Desulfomicrobium, Desulfobulbus, Syntrophobacter, Desulfococcus, Desulfomona, Desulfobacter*, and other fermentative groups. Influence of inorganic ligand availability and organic carbon on the performance of bioreactors and microbial community composition on the treatment of Zn-laden mine water was investigated. The results revealed the removal of zinc in the form of zinc sulfide after few days of treatment and no difference was observed in the microbial community composition of the bioreactors amended with alfalfa and wood chips. Rice bran was used as a carbon source to treat AMD through sulfate-reducing bioreactors (Sato et al. 2018). The results revealed the reduction of sulfate with successful enrichment of SRB member (*Desulforhabdus*), and decrement of metal concentration was observed. Giachini et al. (2018) used the poultry-derived biochar to treat AMD and was successful in the removal of sulfate and metals. Grubb et al. (2018) reported the successful removal of metals (>90%) from AMD with active involvement of SRB members.

8.5.2.2.2 Bioaugmentation or Biostimulation and Bioaugmentation-Based Bioremediation of AMD or Mine Discharge

In contrast to biostimulation, there are several studies where the potential of acidophilic or neutrophilic sulfate-reducing bacteria was used to treat AMD. These sulfate-reducing microbial consortia were developed either from municipal waste/activated anaerobic sludge (Bai et al. 2013; Zhang et al. 2016; Zhang and Wang 2016) or mine environment (Elliott et al. 1998; Jong and Parry 2003; Nancucheo and Johnson 2012; Jing et al. 2018; Gonzalez et al. 2019). Low-pH sulfidogenic bioreactor was operated by acidophilic SRB as these members were capable to perform sulfidogenesis at low pH (Kimura et al. 2006; Nancucheo and Johnson 2012; Johnson and Santos 2018). A detailed list of bioaugmentation- and biostimulation-based treatment studies were tabulated and represented in Table 8.2. The role of SRB-containing consortium in remediation of acidic metal and sulfate-rich water has been successfully demonstrated (Nancucheo et al. 2017). Thiopaq®, by Paques, the Netherlands, and BioSulphide®, developed by BioteQ Environmental Technologies Inc., Canada, are the two patented bioreactors using SRB which are being implemented in various sites including Budelco zinc refinery, the Netherlands;

Gold Mine Pueblo Viejo, Dominican Republic; Kennecott Utah Copper Mine, Utah; and Copper Queen Mine, Bisbee, Arizona, respectively, for AMD remediation and metal recovery (Nancucheo et al. 2017).

8.6 Sulfate-Reducing Bacteria and Their Application in Remediation of Acid Mine Drainage

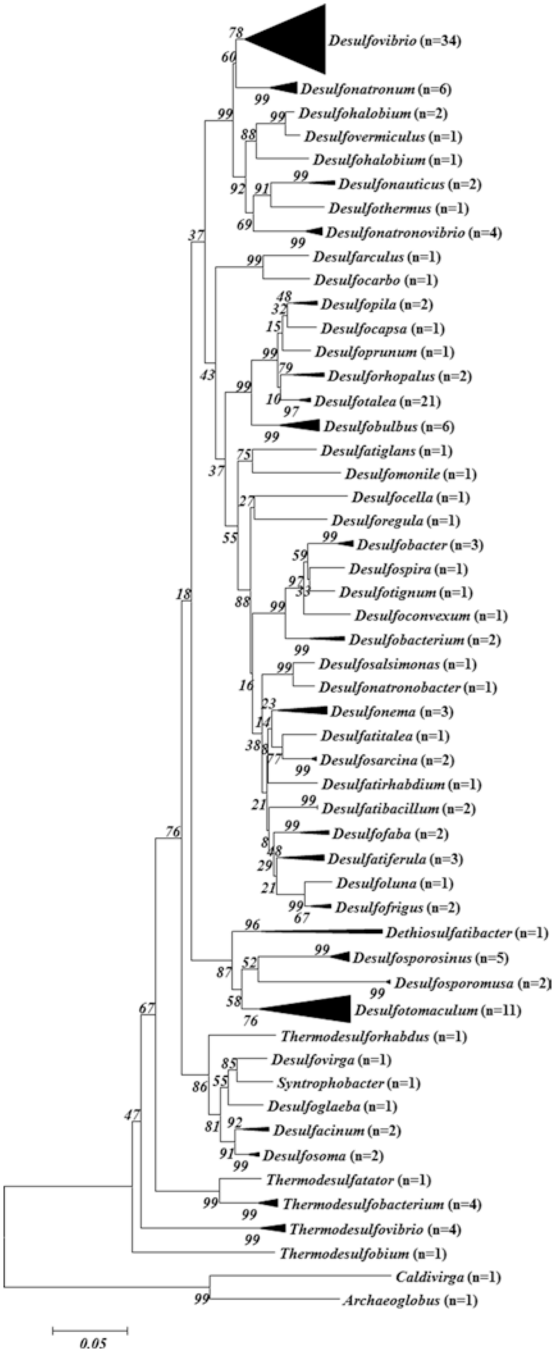
8.6.1 Taxonomy

Sulfate-reducing prokaryotes are anaerobic and utilize sulfate (most oxidized form of sulfur) as their terminal electron acceptor for oxidation of organic compounds (fatty acids, alcohol, hydrocarbon, etc.) and hydrogen (Plugge et al. 2011; Muyzer and Stams 2008). These bacteria are known to play an important role in global carbon and sulfur cycles (Crowe et al. 2014). Sulfate-reducing prokaryotes are mainly present in *Deltaproteobacteria* (subdivision of *Proteobacteria*), while few other members are present in domain of *Nitrospira*, *Thermodesulfobacteria*, *Clostridia*, and *Euryarchaeota/Crenarchaeota* (Stahl et al. 2002; Rabus et al. 2006; Rabus et al. 2013) (Fig. 8.3). Based on rRNA sequence analysis, these SRB can be classified into four major phylogenetic lineages: Gram-negative mesophilic SRB (e.g., *Desulfovibrio, Desulfomonile, Desulfobulbus*), Gram-positive spore-forming SRB (e.g., *Desulfotomaculum*), thermophilic bacterial SRB (e.g., *Thermodesulfobacterium* and *Thermodesulfovibrio*), and thermophilic archaeal SRB (e.g., *Achaeoglobus*) (Castro et al. 2000). Both 16S rRNA and dsrAB (dissimilatory sulfite reductase) genes were used as molecular markers for identification of SRB in any environment. Fingerprinting of *dsr*AB gene through t-RFLP, DGGE, and gel-retardation analyses were used to determine the SRB populations of any ecosystems (Wagner et al. 2005; Geets et al. 2006). It is important to understand the nutritional requirement of diverse SRB to utilize their potential for bioremediation processes.

8.6.2 Metabolic Versatility

Metabolic versatility of SRB is well established in the 1970s (Plugge et al. 2011 and references therein). In the last few decades, several biochemical studies have been conducted to understand their mode of metabolism [autotrophic (grow autotrophically with hydrogen and fixing CO_2), litho-autotrophic (reduced mineral and CO_2), or heterotrophic (utilize organic carbons)], suitable carbon substrates (electron donor), or terminal electron acceptors for efficient growth and energy generation process (Rabus et al. 2006; Fichtel et al. 2012; Hussain and Qazi 2016; Agostino and Rosenbaum 2018; Qian et al. 2018 and references therein). In addition to sulfate, various sulfur species (sulfite, thiosulfate, and tetrathionate) have been used by SRB as terminal electron acceptors (Rabus et al. 2006; Muyzer and Stams 2008). Various carbon compounds can be used by heterotrophic SRB including sugars, amino acids, alcohols monocarboxylic acids, dicarboxylic acids, and aromatic

Fig. 8.3 Neighbor-joining phylogenetic tree based on 16S rRNA gene sequence of type strain of sulfate-reducing taxa at 1000 bootstrap. Scale bar refers to a phylogenetic distance of 0.05 nucleotide substitutions per site. All the sequences of the type strains were recovered from Ribosomal Database Project except for *Caldivirga* and *Archaeoglobus* whose 16S rRNA gene sequences were retrieved from NCBI while n represents the number of type stains used for construction of phylogenetic tr



compounds (Fauque 1995; Fauque and Ollivier 2004; Rabus et al. 2006; Zagury et al. 2007; Muyzer and Stams 2008). Sulfate reducers are known to grow syntrophically with methanogenic populations in both sulfate-rich and sulfate-depleted marine environments for mineralization of organic carbon (Odom and singleton 1993; Raskin et al. 1996; Finke et al. 2007; Xiao et al. 2017). Sulfate-reducing populations coexist with methanogens by competing for common substrates, i.e., hydrogen for their growth and metabolism (Stams and Plugge 2009; Paulo et al. 2015; Ozuolmez et al. 2015). Thus, some SRB showed dual life styles: sulfidogenic and syntrophic metabolism (Plugge et al. 2011). These dual metabolic potentials improve the chance of survival of SRB under sulfate depletion condition.

8.6.3 Dissimilatory Sulfate Reduction Pathway

Sulfate reduction process occurs in three steps: (i) activation of sulfate with two ATP molecules by ATP sulfurylase to generate adenosine phosphosulfate (APS) and pyrophosphate, (ii) reduction of APS into sulfite by APS reductase with release of AMP and consumption of two electrons, and (iii) reduction of sulfite to sulfide. Two mechanisms were proposed for the last step of sulfate reduction: (i) direct pathway, in which sulfite is directly converted to sulfide with the help of bisulfite reductase (Peck and LeGall 1982), and (ii) trithionate pathway, in which sulfite is first converted to trithionate which is further converted into thiosulfate, followed by reduction of thiosulfate to sulfide with the help of sulfite reductase, trithionate reductase, and thiosulfate reductase, respectively (Kobayashi et al. 1969, 1974). Chambers and Trudinger (1975) reported that neither thiosulfate nor trithionate was a normal intermediate in the reduction pathway. Santos et al. (2015) reported that sulfite was first converted to DrsC trisulfide by *dsr*AB/*dsr*C genes which was further reduced to $\mathrm{DsrC_r}$ and sulfide by *dsr*MKJOP complex. They further reported that DsrC was a co-substrate for sulfite reduction by *dsr*AB and absence of DsrC or high bisulfite concentration lead to the production of thiosulfate and trithionate as in vitro products of *dsr*AB. In order to understand the rate of sulfate reduction and sulfate transportation with the formation of different intermediary products intracellularly, isotopic fraction of sulfur was examined to understand the sulfur transfer pathway in dissimilatory sulfate reduction (Sim et al. 2017).

8.6.4 Substrate-Level Phosphorylation

Sulfate-reducing microbes are known to utilize diverse organic carbon for their metabolism. Based on their mode of oxidation, they are categorized into (i) complete oxidizers – which completely oxidize organic carbon to CO_2, and (ii) incomplete oxidizers, which form acetate as an end product on oxidation of organic carbon (Castro et al. 2002). Out of the known SRB species, 70% of the species fall into incomplete oxidation category (Qian et al. 2018).

Lactate is considered to be the most common organic carbon substrate/electron donor for the SRB (Plugge et al. 2011). It is oxidized to pyruvate by a D-or L-lactate dehydrogenase which is ultimately oxidized to acetate. Lactate oxidation yields two molecules of ATP through substrate-level phosphorylation, which are used for activation of sulfate during first step of sulfate reduction pathway resulting in no net gain of ATP. Two hypothetical models are proposed for electron transfer from lactate oxidation to sulfate reduction process: (i) H_2 cycling pathway in which H_2 is produced from cytoplasmic and periplasmic hydrogenases which ultimately transfers electron to terminal reductase via cytochrome and transmembrane complexes (Heidelberg et al. 2004) and (ii) second pathway that transfers electrons from lactate oxidation directly to the membrane-bound menaquinone pool which further transfers the electrons to terminal reductase via transmembrane-bound complexes (Keller and Wall 2011). Citric acid cycle (CAC) and oxidative carbon monoxide dehydrogenase (OCMD) pathways are operated in SRB to completely oxidize the acetate (Goevert and Conrad 2008 and references therein). But most of the organisms utilize OCMD as it operates at more negative redox potential [greater than that of the APS/HSO_3^- couple (-60 mV) and HSO_3^- /HS^- couple (-116 mV)] than CAC pathway (Thauer et al. 2007). Propionate is another electron donor and carbon source for several incomplete and complete SRB (Widdel and Pfennig 1982; Suzuki et al. 2007; El Houari et al. 2017). Methylmalonyl-CoA pathway was considered to be operated in Desulfobulbus propionicus for its incomplete oxidation (Widdel and Pfenning 1982). This pathway was found to be more thermodynamically/energetically favorable than oxidation of propionyl-CoA via acrylyl-CoA, because redox potential of the acrylyl-CoA/propionyl-CoA couple is more positive (+69 mV) than fumarate/succinate couple (þ33 mV) (Barton and Hamilton 2007). The completely oxidizing sulfate reducers use the classical b-oxidation pathway to degrade fatty acids (Janssen and Schink 1995a, b). The electron donor or carbon source plays an important role in the metabolic pathways of SRB. It was reported that several other important organic carbons were utilized by SRB for sulfate reduction. Complex polysaccharides, amino acid/protein, or alcohol enhance the sulfate-reduction ability of SRB (Neculita et al. 2007; Schmidtova and Baldwin 2011; Ayala-Parra et al. 2016; Hussain et al. 2016).

8.6.5 Electron Transport Phosphorylation

Electron transport phosphorylation occurs in SRB where H_2 acts as an electron donor for dissimilatory sulfate reduction. In this pathway, H_2 is oxidized by periplasmic hydrogenase (Hase1) of SRB to generate electron and H^+ ion. The generated electron transfers to cytoplasmic heme type cytochrome C_3, which transfers it to cytoplasmic dissimilatory sulfite reductase via transmembrane complex (da Silva et al. 2013). The H^+ ion generated in this mechanism is pumped across the cytoplasmic membrane with proton motive pump. This results in a H^+ gradient between the cytoplasm and periplasm resulting in the generation of ATP through phosphorylation of ADP with the help of membrane-bound ATP synthase (Fitz and Cypionka

1991). Odom and Peck (1981) reported the production of H_2 during the growth of *Desulfovibrio* species on lactate/sulfate media. But genetic evidence confirmed that H_2 cycling in *Desullfovibrio alaskensis* G20 mutant of type 1 cytochrome c3, *Desulfovibrio vulgaris* Hildenborough, mutants of Tp1-c3, *Desulfovibrio gigas* mutants of cytoplasmic hydrogenase or periplasmic hydrogenase, was not required for sulfate reduction (Heidelberg et al. 2004; Li et al. 2009; Keller and wall 2011; Sim et al. 2013; Morais-Silva et al. 2013; Keller et al. 2014; Price et al. 2014). Another potential mechanism for electron-transport phosphorylation is formate cycling. Heidelberg et al. (2004) reported that in *Desulfovibrio vulgaris* Hildenborough, formate is oxidized by formate dehydrogenases present in the periplasm. A putative cytoplasmic formate: hydrogen lyase was reported from the genome of *D. alaskensis* G20 which could convert cytoplasmic formic acid to H_2 and CO_2 or vice versa (Pereira et al. 2011). Electrons generated from the oxidation of formate can be transferred to cytoplasmic membrane for sulfate reduction via periplasmic electron carriers and the produced H^+ ion creates a gradient across the membrane for ATP generation. Knockout of *Desulfovibrio vulgaris* Hildenborough for formate dehydrogenase showed reduced growth in lactate/sulfate media indicated the role of formate cycling in energy production (da Silva et al. 2013). In a cycA mutant of *Desulfovibrio alaskensis* G20, accumulation of formate was observed on lactate/sulfate media which suggested that formate formed during oxidation of lactate oxidation was immediately reoxidized. (Li et al. 2009). There are several transmembrane redox complexes such as Qrc complex, Qmo complex, DsrMKJOP complex, Hmc (high-molecular weight cytochrome) and Tmc (with a periplasmic type II cytochrome c3 subunit), Hdr/flox, nfn, and Rnf identified in SRB which are known to be involved in electron transfer to cytoplasm (Pereira et al. 1998, 2006; Li et al. 2009; Venceslau et al. 2010; Grein et al. 2010; Pereira et al. 2011; Ramos et al. 2012; Quintas et al. 2013; Keller et al. 2014; Meyer et al. 2014).

8.6.6 Extracellular Electron Transfer Between ANME and SRB

Anaerobic methane oxidation by archaeal members in association with sulfate-reducing bacteria offers extracellular electron transfer to SRB for dissimilatory sulfate reduction process (Boetius et al. 2000). Various studies have been conducted to understand the genetic potential of ANME archaea and syntrophic association with SRB members (Skennerton et al. 2017 and references therein). The two possible mechanisms of methane oxidation coupled with sulfate reduction were proposed (Milucka et al. 2012; McGlynn et al. 2015; Wegener et al. 2015; Scheller et al. 2016; Skennerton et al. 2017). Wegener et al. (2015) suggested that under thermophilic anaerobic methane oxidation (TAOM) conditions, both ANME and the HotSeep-1 bacteria overexpressed the extracellular cytochrome production genes and formed cell-to-cell connections by expressing the genes for pili production which is responsible for interspecies electron transfer between syntrophic consortia. In contrast to the previous mechanism, Milucka et al. (2012) confirmed that ANME-2 oxidized methane with a concomitant reduction of sulphate to zero-valent sulfur for extracellular electron transfer. Hence, it can be concluded that AOM is not an obligate syntrophic process. Produced S^0 is exported outside the cell where it reacts with sulfide to form disulfide. Disulfide is disproportionated to sulfate and sulfide by sulfate-reducing Deltaproteobacterial members.

8.6.7 SRB in Acidic Condition and Factors Affecting SRB Activities

It was believed that SRB thrive in environmental conditions above pH 5.0 (Hao et al. 1996). In the last decades, several studies confirmed the possibility of sulfate reduction at low pH condition ($pH < 5.0$) (Sánchez-Andrea et al. 2014). The presence of SRB in acidic environment has been reported in several AMD sites and was suggested that the existence of micro-niches of higher pH in such environments supported the growth and metabolism of SRB (Sánchez-Andrea et al. 2014 and references therein). It is reported that low pH destabilizes the macromolecules (proteins get denatured), changes the conformation of surface protein due to protonation as well as increases energy cost for pH homeostasis (Golyshina and Timmis 2005; Krulwich et al. 2011). Acidophilic organisms have different strategies to maintain the circum-neutral pH in the cytosol by pumping out the H+ ion, changing the permeability of membrane, increasing the positive redox potential of cytoplasm through potassium transporter, and decarboxylation of amino acids (Chen et al. 2015 and references therein). At low pH, H_2S and organic acids are also toxic to SRB (Koschorreck 2008). Sulfate reduction process generates H_2S as the main product, which remains freely present in undissociated form at $pH < 5.0$ (Moosa and Harrison 2006). Furthermore, it has a negative impact on cells due its toxic nature as well as high membrane permeability. There are several reports where inhibition of sulfate reduction with increase in sulfiide concentration was observed (Reis et al. 1992; Icgen and Harrison 2006; Koschorreck 2008; Cassidy et al. 2015 and references therein). Similarly, low molecular weight organic compounds such as acetate and lactate are mostly in undissociated state at low pH, which may pass the cell membrane and get dissociated inside the cytoplasm releasing proton which in turn lowers the pH (Sanchez-Andrea et al. 2014 and references therein). The nonionic substrates such as glycerol, hydrogen, and ethanol were more preferred at low pH (Nagpal et al. 2000; Kaksonen et al. 2004; Bijmans et al. 2009). Benner et al. 1999 reported that anaerobic bacteria change their mode of carbohydrate metabolism to avoid the accumulation of organic acid inside the cytoplasm at low pH condition. There are reports where SRB activity decreases with increasing undissociated concentration of lactate or acetate (Reis et al. 1990; Jong and Parry 2006). Other than the above-mentioned factors, several other factors are known to be inhibitory for sulfate-reducing taxa. Heavy metals are considered to be toxic to several SRB above certain threshold (Utgikar et al. 2002; Sani et al. 2001). Effect of copper toxicity on sulfate removal efficiency was observed and found that 1.57mM copper concentration reduced the efficiency of SRB for sulfate removal to 50% (Song et al. 1998). Sani et al. 2001 showed the toxic effects of copper, zinc, and lead on *Desulfovibrio desulfurican* G20. It was found that at copper concentration of 13.3uM, specific growth rate of *D. desulfurican* G20 got reduced to 50%. In another study 10uM concentration of lead was shown as minimum inhibitory concentration for *Desulfovibrio desulfurican* G20 at pH 6.0 (Sani et al. 2003). These studies suggest that heavy metals increased the lag phase and lower the specific growth rates of the tested species. Toxic effects of several heavy metals [Cu(II), Zn(II)], Mn(II), Ni(II), and Cr(III)] were evaluated through batch studies on two SRB cultures, *Desulfovibrio vulgaris and Desulfovibrio* sp (Cabrera et al. 2006 and references therein). The results indicated Cu > Ni > Mn > Cr > Zn showed maximum inhibitory effect on both the SRB cultures. Higher concentration of molybdate may act as an inhibitor for sulfate reduction as it is a structural analog of sulfate (Biswas et al. 2009; de Jesus et al. 2015). Hussain and Qazi (2016) reported that higher concentration (10 and 15 ppm) of Cu, Cr, and Ni inhibited bioprecipitation and sulphate reduction by *Desulfotomaculum reducens*-HA1 and *Desulfotomaculum hydrothermale*-HA2. It was reported that sulfate reduction could not be observed at oxic condition or in the presence of nitrate and nitrite (Rubio-Rincón et al. 2017). It was suggested that nitrite formation by nitrate inhibited the SRB activities, because nitrite suppressed the sulfate reduction (Barton and Hamilton 2007; Mohanakrishnan et al. 2008). SRB are known to reduce oxygen as a protective mechanism against its harmful effects (Lamrabet et al. 2011 and reference therein).

8.6.8 Resource Recovery from AMD Treatment Using SRB

Sulfate-reducing bacteria are known to have diverse metabolic properties and have been used in various treatment processes. The ability of SRB to produce biohydrogen, aliphatic hydrocarbon, polyhydroxyalkanoates (PHA), magnetite, and metal sulfides is well documented (Gramp et al. 2007; Gramp et al. 2010; Yu et al. 2011; Peltier et al. 2011; Friedman and Rude 2012; Martins and Pereira 2013; Hai et al. 2004; Hedrich and Johnson 2014; Martins et al. 2015). Sulfate reducers are capable of oxidizing various organic carbons and produce sulfide as the main product of sulfate reduction. Interaction of sulfide with the metals such as Fe, Cu, Ni, Zn, and Cd lead to the formation of metal sulfides. Sulfidogenic treatment of AMD leads to generation of metal sulfide, and also the generated sulfide could be used for the production of elemental sulfur via oxidation (aeration) (Nancucheo et al. 2017). There are two strategies generally used for metal sulfide production during treatment of AMD: (i) direct interaction of sulfide and metals (in-line sulfidogenic reactors) and (ii) sulfide produced during the sulfidogenesis is separated and used as a metal precipitating agent (offline sulfidogenic reactors). Thioteq (Paques) and BioSulfide (BioteQ) are the two offline sulfidogenic systems used for metal recovery from the AMD/wastewater treatment. Biogenic Ni and Zn sulfide precipitation were observed during the growth of SRB in Ni- and Zn-containing medium (Gramp et al. 2007). The Ni-sulfidic phase (Heazelwoodite) was more crystalline than its abiotic control setup. Gramp et al. (2009) reported the formation of iron sulfides (mackinawite and greigite) by the sulfate-reducing bacteria, and with the increase in incubation temperature of the bacteria, crystallinity of the iron sulfides got enhanced.

Castillo et al. (2012) observed the zinc precipitation in the two polymorphs of ZnS (sphalerite and wurztite) while investigating the tolerance of SRB against zinc-rich sulfate medium for the application of SRB in AMD remediation. Hedrich and Johnson (2014) used the modular bioreactor for the recovery of metal sulfide (ZnS) during the treatment of metal-containing wastewaster. Zhou et al. (2014) reported the iron sulfide precipitation during the extended incubation of *Desulfovibrio vulgaris,* and higher sulfide accumulation led to the transformation of mackinawte to gregite. Murray et al. (2017) reported the use of waste H_2S gas from AMD remediation to synthesize zinc sulfide quantum dots, which was found to be different in its physical and optical properties from its other chemical counterparts. Picard et al. (2018) reported that *Desulfovibrio hydrothermalis* AM13 influenced the nucleation and growth of iron sulfidic minerals. Overall, metal sulfides are known to have diverse applications including cancer therapy, antimicrobial agents, textile, opto-electronics, hydro-cracking in fuel refineries, and hydro-processing (Qian et al. 2018 and references therein).

8.7 Conclusion

The toxic and lethal effects of AMD or acidic mine water on environmental health are of major concern. This problem has gained attention from the researchers to find out a promising technology for its treatment or measures to prevent its generation. There are several prevention measures through which its generation can be checked, but several factors limit these options. There are remediation technologies being used including both passive and active treatment strategies. But the choice of remediation technologies depends upon various factors such as (i) mine type, (ii) type of waste generated, (iii) geochemistry of AMD, (iv) cost of the treatment system, and (v) sustainability and long-term treatment options. Due to high capital investment, requirement of large area, continuous input of neutralization agents, sludge accumulation and its disposal, as well as sustainability of chemical treatment options, biological treatments are found to be more attractive nowadays. Biological treatment provides cost-effective, sustainable, and eco-friendly options to treat AMD and recover metals from the AMD environment. Advancement in the molecular approaches allowed the researchers to gain a deeper insight of microbial community and composition, their functions, and interaction in such processes. Sulfidogenic activity and metabolic versatility of SRB play an important role in attenuation of AMD and metal precipitation. In future, research is needed to develop this biological technology for its application in more promising ways to treat AMD or AMD-impacted areas.

Acknowledgments Authors are grateful to the Department of Biotechnology, Government of India, for funding the AMD-related project (BT/PR 7533/BCE/8/959/2013, Dated 10/12/2013). AG thanks the Department of Biotechnology, Government of India, for providing fellowship under DBT-JRF category (DBT/2014/IITKH/113).

References

Acai P, Sorrenti E, Polakovič M, Kongolo M, Donato PD (2009) Pyrite passivation by humic acid investigated by inverse liquid chromatography. Colloid Surface Physicochem Eng Asp 337:39–46

Adams R, Ahlfeld D, Sengupta A (2007) Investigating the potential for ongoing pollution from an abandoned pyrite mine. Mine Water Environ 26(1):2–13

Agostino V, Rosenbaum MA (2018) Sulfate-reducing electroautotrophs and their applications in bioelectrochemical systems. Front Energy Res 6:55

Alhamed M, Wohnlich S (2014) Environmental impact of the abandoned coal mines on the surface water and the groundwater quality in the south of Bochum, Germany. Environ Earth Sci 72(9):3251–3267

Arnold DE (1991) Diversion wells–a low-cost approach to treatment of acid mine drainage. In: Proceedings, twelfth west Virginia surface mine drainage task force symposium, pp 3–4

Ayala-Parra P, Sierra-Alvarez R, Field JA (2016) Algae as an electron donor promoting sulfate reduction for the bioremediation of acid rock drainage. J Hazard Mater 317:335–343

Backes CA, Pulford ID, Duncan HJ (1987) Studies on the oxidation of pyrite in colliery spoil. II Inhibition of the oxidation by amendment treatments. Reclamation Revegetation Res 6(1):1–11

Bai H, Kang Y, Quan H, Han Y, Sun J, Feng Y (2013) Treatment of acid mine drainage by sulfate reducing bacteria with iron in bench scale runs. Bioresour Technol 128:818–822

Baker BJ, Banfield JF (2003) Microbial communities in acid mine drainage. FEMS Microbiol Ecol 44(2):139–152

Barton LL, Hamilton WA (eds) (2007) Sulphate-reducing bacteria: environmental and engineered systems. Cambridge University Press, Cambridge

Bayrakdar A, Sahinkaya E, Gungor M, Uyanik S, Atasoy AD (2009) Performance of sulfidogenic anaerobic baffled reactor (ABR) treating acidic and zinc-containing wastewater. Bioresour Technol 100(19):4354–4360

Becerra CA, López-Luna EL, Ergas SJ, Nüsslein K (2009) Microcosm-based study of the attenuation of an acid mine drainage-impacted site through biological sulfate and iron reduction. Geomicrobiol J 26(1):9–20

Behum PT, Lefticariu L, Bender KS, Segid YT, Burns AS, Pugh CW (2011) Remediation of coal-mine drainage by a sulfate-reducing bioreactor: a case study from the Illinois coal basin, USA. Appl Geochem 26:S162–S166

Bekmezci OK, Ucar D, Kaksonen AH, Sahinkaya E (2011) Sulfidogenic biotreatment of synthetic acid mine drainage and sulfide oxidation in anaerobic baffled reactor. J Hazard Mater 189(3):670–676

Benner SG, Blowes DW, Ptacek CJ (1997) A full-scale porous reactive wall for prevention of acid mine drainage. Groundwater Monit Remediation 17(4):99–107

Benner SG, Blowes DW, Gould WD, Herbert RB, Ptacek CJ (1999) Geochemistry of a permeable reactive barrier for metals and acid mine drainage. Environ Sci Technol 33(16):2793–2799

Benzaazoua M, Bussière B, Kongolo M, McLaughlin J, Marion P (2000) Environmental desulphurization of four Canadian mine tailings using froth flotation. Int J Miner Process 60(1):57–74

Bijmans MF, Dopson M, Peeters TW, Lens PN, Buisman CJ (2009) Sulfate reduction at pH 5 in a high-rate membrane bioreactor: reactor performance and microbial community analyses. J Microbiol Biotechnol 19(7):698–708

Biswas KC, Woodards NA, Xu H, Barton LL (2009) Reduction of molybdate by sulfate-reducing bacteria. Biometals 22(1):131–139

Black C, Ziemkiewicz P, Skousen J (1999) Construction of a limestone leach bed and preliminary water quality results in Beaver Creek. In: Proceedings of the 20th West Virginia surface mine drainage task force symposium, Morgantown, WV

Blowes DW, Ptacek CJ, Benner SG, McRae CW, Bennett TA, Puls RW (2000) Treatment of inorganic contaminants using permeable reactive barriers. J Contam Hydrol 45(1–2):123–137

Boetius A, Ravenschlag K, Schubert CJ, Rickert D, Widdel F, Gieseke A, Amann R, Jørgensen BB, Witte U, Pfannkuche O (2000) A marine microbial consortium apparently mediating anaerobic oxidation of methane. Nature 407(6804):623–626

Brown DJA, Sadler K (1989) Fish survival in acid waters. Acid Toxic Aquat Anim 34:31–44

Burns AS, Pugh CW, Segid YT, Behum PT, Lefticariu L, Bender KS (2012) Performance and microbial community dynamics of a sulfate-reducing bioreactor treating coal generated acid mine drainage. Biodegradation 23(3):415–429

Buzzi DC, Viegas LS, Rodrigues MAS, Bernardes AM, Tenório JAS (2013) Water recovery from acid mine drainage by electrodialysis. Miner Eng 40:82–89

Cabrera G, Pérez R, Gomez JM, Abalos A, Cantero D (2006) Toxic effects of dissolved heavy metals on Desulfovibrio vulgaris and Desulfovibrio sp. strains. J Hazard Mater 135(1–3):40–46

Canty GA (1999) Utilization of coal combustion by-products for in situ treatment of acidic mine waters (Doctoral dissertation)

Casiot C, Egal M, Elbaz-Poulichet F, Bruneel O, Bancon-Montigny C, Cordier MA et al (2009) Hydrological and geochemical control of metals and arsenic in a Mediterranean river contaminated by acid mine drainage (the Amous River, France); preliminary assessment of impacts on fish (Leuciscus cephalus). Appl Geochem 24(5):787–799

Cassidy J, Lubberding HJ, Esposito G, Keesman KJ, Lens PN (2015) Automated biological sulphate reduction: a review on mathematical models, monitoring and bioprocess control. FEMS Microbiol Rev 39(6):823–853

Castillo J, Pérez-López R, Caraballo MA, Nieto JM, Martins M, Costa MC et al (2012) Biologically-induced precipitation of sphalerite–wurtzite nanoparticles by sulfate-reducing bacteria: implications for acid mine drainage treatment. Sci Total Environ 423:176–184

Castro HF, Williams NH, Ogram A (2000) Phylogeny of sulfate-reducing bacteria. FEMS Microbiol Ecol 31(1):1–9

Castro H, Reddy KR, Ogram A (2002) Composition and Function of Sulfate-Reducing Prokaryotes in Eutrophic and Pristine Areas of the Florida Everglades. Appl Environ Microbiol 68(12):6129–6137

Chambers LA, Trudinger PA (1975) Are thiosulfate and trithionate intermediates in dissimilatory sulfate reduction? J Bacteriol 123(1):36–40

Chen LX, Hu M, Huang LN, Hua ZS, Kuang JL, Li SJ, Shu WS (2015) Comparative metagenomic and metatranscriptomic analyses of microbial communities in acid mine drainage. ISME J 9(7):1579

Chen LX, Huang LN, Mendez-Garcia C, Kuang JL, Hua ZS, Liu J, Shu WS (2016) Microbial communities, processes and functions in acid mine drainage ecosystems. Curr Opin Biotechnol 38:150–158

Chibuike GU, Obiora SC (2014) Heavy metal polluted soils: effect on plants and bioremediation methods. Appl Environ Soil Sci 2014:708–752

Chon HT, Hwang JH (2000) Geochemical characteristics of the acid mine drainage in the water system in the vicinity of the Dogye coal mine in Korea. Environ Geochem Health 22(2):155–172

Church CD, Wilkin RT, Alpers CN, Rye RO, McCleskey RB (2007) Microbial sulfate reduction and metal attenuation in pH 4 acid mine water. Geochem Trans 8(1):10

Clarke AM, Kirby R, Rose PD (2004) Molecular microbial ecology of lignocellulose mobilisation as a carbon source in mine drainage wastewater treatment. Water SA 30(5):558–661

Clyde EJ, Champagne P, Jamieson HE, Gorman C, Sourial J (2016) The use of a passive treatment system for the mitigation of acid mine drainage at the Williams Brothers Mine (California): pilot-scale study. J Clean Prod 130:116–125

Coggon M, Becerra CA, Nüsslein K, Miller K, Yuretich R, Ergas SJ (2012) Bioavailability of jarosite for stimulating acid mine drainage attenuation. Geochim Cosmochim Acta 78:65–76

Cravotta CA (2007) Passive aerobic treatment of net-alkaline, iron-laden drainage from a flooded underground anthracite mine, Pennsylvania, USA. Mine Water Environ 26(3):128–149

Cravotta CA III (2008a) Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 1: constituent quantities and correlations. Appl Geochem 23(2):166–202

Cravotta CA III (2008b) Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 2: geochemical controls on constituent concentrations. Appl Geochem 23(2):203–226

Cravotta CA, Ward SJ (2008) Downflow limestone beds for treatment of net-acidic, oxic, iron-laden drainage from a flooded anthracite mine, Pennsylvania, USA: 1. Field evaluation. Mine Water Environ 27(2):67–85

Crowe SA, Paris G, Katsev S, Jones C, Kim ST, Zerkle AL, Farquhar J (2014) Sulfate was a trace constituent of Archean seawater. Science 346(6210):735–739

da Silva SM, Voordouw J, Leitao C, Martins M, Voordouw G, Pereira IA (2013) Function of formate dehydrogenases in Desulfovibrio vulgaris Hildenborough energy metabolism. Microbiology 159(8):1760–1769

de Jesus EB, de Andrade Lima LRP, Bernardez LA, Almeida PF (2015) Inhibition of microbial sulfate reduction by molybdate. Braz J Petrol Gas 9(3):95–106

de Mello JWV, Dias LE, Daniel AM, Abrahão WAP, Deschamps E, Schaefer CEGR (2006) Preliminary evaluation of acid mine drainage in Minas Gerais State, Brazil. Rev Bras Ciênc Solo 30(2):365–375

Demers I, Bussière B, Benzaazoua M, Mbonimpa M, Blier A (2008) Column test investigation on the performance of monolayer covers made of desulphurized tailings to prevent acid mine drainage. Miner Eng 21(4):317–329

Deng D, Weidhaas JL, Lin LS (2016) Kinetics and microbial ecology of batch sulfidogenic bioreactors for co-treatment of municipal wastewater and acid mine drainage. J Hazard Mater 305:200–208

Diaby N, Dold B, Pfeifer HR, Holliger C, Johnson DB, Hallberg KB (2007) Microbial communities in a porphyry copper tailings impoundment and their impact on the geochemical dynamics of the mine waste. Environ Microbiol 9(2):298–307

Drennan DM, Almstrand R, Ladderud J, Lee I, Landkamer L, Figueroa L, Sharp JO (2017) Spatial impacts of inorganic ligand availability and localized microbial community structure on mitigation of zinc laden mine water in sulfate-reducing bioreactors. Water Res 115:50–59

El Houari A, Ranchou-Peyruse M, Ranchou-Peyruse A, Dakdaki A, Guignard M, Idouhammou L, Qatibi AI (2017) Desulfobulbus oligotrophicus sp. nov., a sulfate-reducing and propionate-oxidizing bacterium isolated from a municipal anaerobic sewage sludge digester. Int J Syst Evol Microbiol 67(2):275–281

Elliott P, Ragusa S, Catcheside D (1998) Growth of sulfate-reducing bacteria under acidic conditions in an upflow anaerobic bioreactor as a treatment system for acid mine drainage. Water Res 32(12):3724–3730

Elsetinow AR, Borda MJ, Schoonen MA, Strongin DR (2003) Suppression of pyrite oxidation in acidic aqueous environments using lipids having two hydrophobic tails. Adv Environ Res 7(4):969–974

Equeenuddin SM, Tripathy S, Sahoo PK, Panigrahi MK (2010) Hydrogeochemical characteristics of acid mine drainage and water pollution at Makum Coalfield, India. J Geochem Explorat 105(3):75–82

Faulkner BB, Skousen JG (1994) Treatment of acid mine drainage by passive treatment systems. Int Land Reclam Mine Drain Conf 2:250–257

Fauque GD (1995) Ecology of sulfate-reducing bacteria. In: Sulfate-reducing bacteria. Springer, Boston, pp 217–241

Fauque G, Ollivier B (2004) Anaerobes: the sulfate-reducing bacteria as an example of metabolic diversity. In: Microbial diversity and bioprospecting. American Society of Microbiology, Washington, DC, pp 169–176

Fenalcarbón (2006) Acuerdo de concertación para la producción mas limpia de la minería de carbón subterráneo. Federacion Nacional de Carboneros

Feng D, Aldrich C, Tan H (2000) Treatment of acid mine water by use of heavy metal precipitation and ion exchange. Miner Eng 13(6):623–642

Fichtel K, Mathes F, Könneke M, Cypionka H, Engelen B (2012) Isolation of sulfate-reducing bacteria from sediments above the deep-subseafloor aquifer. Front Microbiol 3:65

Finke N, Hoehler TM, Jørgensen BB (2007) Hydrogen 'leakage'during methanogenesis from methanol and methylamine: implications for anaerobic carbon degradation pathways in aquatic sediments. Environ Microbiol 9(4):1060–1071

Fitz RM, Cypionka H (1991) Generation of a proton gradient in Desulfovibrio vulgaris. Arch Microbiol 155(5):444–448

Friedman L, Rude M (2012) U.S. Patent No. 8,110,093. U.S. Patent and Trademark Office, Washington, DC

Garrido AE, Condori J, Strosnider WH, Nairn RW (2009) Acid mine drainage impacts on irrigation water resources, agricultural soils, and potatoes in Potosi, Bolivia. In: Proceedings America Society of Mining and Reclamation, pp 486–499

Geets J, Borremans B, Diels L, Springael D, Vangronsveld J, Van Der Lelie D, Vanbroekhoven K (2006) DsrB gene-based DGGE for community and diversity surveys of sulfate-reducing bacteria. J Microbiol Methods 66(2):194–205

Gerhardt A, De Bisthoven LJ, Soares AMVM (2004) Macroinvertebrate response to acid mine drainage: community metrics and on-line behavioural toxicity bioassay. Environ Pollut 130(2):263–274

Giachini AJ, Sulzbach TS, Pinto AL, Armas RD, Cortez DH, Silva EP et al (2018) Microbially-enriched poultry litter-derived biochar for the treatment of acid mine drainage. Arch Microbiol 200(8):1227–1237

Gibert O, De Pablo J, Cortina JL, Ayora C (2004) Chemical characterisation of natural organic substrates for biological mitigation of acid mine drainage. Water Res 38(19):4186–4196

Gibert O, de Pablo J, Cortina JL, Ayora C (2005) Municipal compost-based mixture for acid mine drainage bioremediation: metal retention mechanisms. Appl Geochem 20(9):1648–1657

Gibert O, Rötting T, Cortina JL, de Pablo J, Ayora C, Carrera J, Bolzicco J (2011) In-situ remediation of acid mine drainage using a permeable reactive barrier in Aznalcollar (Sw Spain). J Hazard Mater 191(1–3):287–295

Giller KE, Amijee F, Brodrick SJ, Edje OT (1998) Environmental constraints to nodulation and nitrogen fixation of Phaseolus vulgaris L in Tanzania II. Response to N and P fertilizers and inoculation with Rhizobium. Afr Crop Sci J 6(2):171–178

Goevert D, Conrad R (2008) Carbon isotope fractionation by sulfate-reducing bacteria using different pathways for the oxidation of acetate. Environ Sci Technol 42(21):7813–7817

Golab AN, Peterson MA, Indraratna B (2006) Selection of potential reactive materials for a permeable reactive barrier for remediating acidic groundwater in acid sulphate soil terrains. Q J Eng Geol Hydrogeol 39(2):209–223

Golyshina OV, Timmis KN (2005) Ferroplasma and relatives, recently discovered cell wall-lacking archaea making a living in extremely acid, heavy metal-rich environments. Environ Microbiol 7(9):1277–1288

González D, Liu Y, Gomez DV, Southam G, Hedrich S, Galleguillos P et al (2019) Performance of a sulfidogenic bioreactor inoculated with indigenous acidic communities for treating an extremely acidic mine water. Miner Eng 131:370–375

Gramp JP, Bigham JM, Sasaki K, Tuovinen OH (2007) Formation of Ni-and Zn-sulfides in cultures of sulfate-reducing bacteria. Geomicrobiol J 24(7–8):609–614

Gramp JP, Wang H, Bigham JM, Jones FS, Tuovinen OH (2009) Biogenic synthesis and reduction of Fe (III)-hydroxysulfates. Geomicrobiol J 26(4):275–280

Gramp JP, Bigham JM, Jones FS, Tuovinen OH (2010) Formation of Fe-sulfides in cultures of sulfate-reducing bacteria. J Hazard Mater 175(1–3):1062–1067

Grande JA, Santisteban M, de la Torre ML, Dávila JM, Pérez-Ostalé E (2018) Map of impact by acid mine drainage in the river network of The Iberian Pyrite Belt (Sw Spain). Chemosphere 199:269–277

Gray NF (1997) Environmental impact and remediation of acid mine drainage: a management problem. Environ Geol 30(1–2):62–71

Gray NF, Delaney E (2008) Comparison of benthic macroinvertebrate indices for the assessment of the impact of acid mine drainage on an Irish river below an abandoned Cu–S mine. Environ Pollut 155(1):31–40

Grein F, Venceslau SS, Schneider L, Hildebrandt P, Todorovic S, Pereira IA, Dahl C (2010) DsrJ, an essential part of the DsrMKJOP transmembrane complex in the purple sulfur bacterium Allochromatium vinosum, is an unusual triheme cytochrome c. Biochemistry 49(38):8290–8299

Grubb DG, Landers DG, Guerra PA, Miller B, Bilgin A, Hernandez MT (2018) Sugarcane bagasse as a microbial host media for the passive treatment of acid mine drainage. J Environ Eng 144(10):04018108

Gupta SK, Nikhil K (2016) Ground water contamination in coal mining areas: a critical review. Int J Eng Appl Sci 3(2):295–304

Gupta A, Dutta A, Sarkar J, Panigrahi MK, Sar P (2018) Low-abundance members of the firmicutes facilitate bioremediation of soil impacted by highly acidic mine drainage from the Malanjkhand copper project, India. Front Microbiol 9:2882

Hai T, Lange D, Rabus R, Steinbüchel A (2004) Polyhydroxyalkanoate (PHA) accumulation in sulfate-reducing bacteria and identification of a class III PHA synthase (PhaEC) in Desulfococcus multivorans. Appl Environ Microbiol 70(8):4440–4448

Hao OJ, Chen JM, Huang L, Buglass RL (1996) Sulfate-reducing bacteria. Crit Rev Environ Sci Technol 26(2):155–187

Hao J, Murphy R, Lim E, Schoonen MA, Strongin DR (2009) Effects of phospholipid on pyrite oxidation in the presence of autotrophic and heterotrophic bacteria. Geochim Cosmochim Acta 73(14):4111–4123

Hao TW, Xiang PY, Mackey HR, Chi K, Lu H, Chui HK, Chen GH (2014) A review of biological sulfate conversions in wastewater treatment. Water Res 65:1–21

Harrison JM (2005) Ferric iron and sulfate reduction in the attenuation of acid mine drainage: a microcosm study (Doctoral dissertation, MS Thesis, Department of Civil and Environmental Engineering, University of Massachusetts-Amherst, 144p)

He L, Gao B, Luo X, Jiao J, Qin H, Zhang C, Dong Y (2018) Health risk assessment of heavy metals in surface water near a uranium tailing pond in Jiangxi Province, south China. Sustainability 10(4):1113

Hedrich S, Johnson DB (2014) Remediation and selective recovery of metals from acidic mine waters using novel modular bioreactors. Environ Sci Technol 48(20):12206–12212

Heidelberg JF, Seshadri R, Haveman SA, Hemme CL, Paulsen IT, Kolonay JF et al (2004) The genome sequence of the anaerobic, sulfate-reducing bacterium Desulfovibrio vulgaris Hildenborough. Nat Biotechnol 22(5):554

Hesketh AH, Broadhurst JL, Harrison STL (2010) Mitigating the generation of acid mine drainage from copper sulfide tailings impoundments in perpetuity: a case study for an integrated management strategy. Miner Eng 23(3):225–229

Hiibel SR, Pereyra LP, Inman LY, Tischer A, Reisman DJ, Reardon KF, Pruden A (2008) Microbial community analysis of two field-scale sulfate-reducing bioreactors treating mine drainage. Environ Microbiol 10(8):2087–2097

Hiibel SR, Pereyra LP, Breazeal MVR, Reisman DJ, Reardon KF, Pruden A (2011) Effect of organic substrate on the microbial community structure in pilot-scale sulfate-reducing biochemical reactors treating mine drainage. Environ Eng Sci 28(8):563–572

Hogsden KL, Harding JS (2011) Consequences of acid mine drainage for the structure and function of benthic stream communities: a review. Freshwat Sci 31(1):108–120

Huang X, Evangelou VP (1994) Suppression of pyrite oxidation rate by phosphate addition. In: Alper CN, Blowes DW (eds) Environmental geochemistry of sulfide oxidation. American Chemical Society, Washington, DC

Hussain A, Qazi JI (2016) Metals-induced functional stress in sulphate-reducing thermophiles. 3 Biotech 6(1):17

Hussain A, Hasan A, Javid A, Qazi JI, (2016) Exploited application of sulfate-reducing bacteria for concomitant treatment of metallic and non-metallic wastes: a mini review. 3 Biotech 6(2)

Hwang SK, Jho EH (2018) Heavy metal and sulfate removal from sulfate-rich synthetic mine drainages using sulfate reducing bacteria. Sci Total Environ 635:1308–1316

Icgen B, Harrison S (2006) Exposure to sulfide causes populations shifts in sulfate-reducing consortia. Res Microbiol 157(8):784–791

Jaishankar M, Tseten T, Anbalagan N, Mathew BB, Beeregowda KN (2014) Toxicity, mechanism and health effects of some heavy metals. Interdiscip Toxicol 7(2):60–72

Jameson E, Rowe OF, Hallberg KB, Johnson DB (2010) Sulfidogenesis and selective precipitation of metals at low pH mediated by Acidithiobacillus spp. and acidophilic sulfate-reducing bacteria. Hydrometallurgy 104(3–4):488–493

Janssen PH, Schink B (1995a) Catabolic and anabolic enzyme activities and energetics of acetone metabolism of the sulfatereducing bacterium Desulfococcus biacutus. J Bacteriol 177:277–282

Janssen PH, Schink B (1995b) Pathway of butyrate catabolism by Desulfobacterium cetonicum. J Bacteriol 177:3870–3872

Jennings SR, Blicker PS, Neuman DR (2008) Acid mine drainage and effects on fish health and ecology: a review. Reclamation Research Group, Bozeman

Jin S, Fallgren PH, Morris JM, Gossard RB (2008) Biological source treatment of acid mine drainage using microbial and substrate amendments: microcosm studies. Mine Water Environ 27(1):20–30

Jing Q, Zhang M, Liu X, Li Y, Wang Z, Wen J (2018) Bench-scale microbial remediation of the model acid mine drainage: effects of nutrients and microbes on the source bioremediation. Int Biodeterior Biodegradation 128:117–121

Johnson DB (2012) Geomicrobiology of extremely acidic subsurface environments. FEMS Microbiol Ecol 81(1):2–12

Johnson DB, Hallberg KB (2005a) Acid mine drainage remediation options: a review. Sci Total Environ 338(1–2):3–14

Johnson DB, Hallberg KB (2005b) Biogeochemistry of the compost bioreactor components of a composite acid mine drainage passive remediation system. Sci Total Environ 338(1–2):81–93

Johnson DB, Santos AL (2018) Design and application of a low pH upflow biofilm sulfidogenic bioreactor for recovering transition metals from synthetic waste water at a Brazilian copper mine. Front Microbiol 9:2051

Jong T, Parry DL (2003) Removal of sulfate and heavy metals by sulfate reducing bacteria in short-term bench scale upflow anaerobic packed bed reactor runs. Water Res 37(14):3379–3389

Jong T, Parry DL (2006) Microbial sulfate reduction under sequentially acidic conditions in an upflow anaerobic packed bed bioreactor. Water Res 40(13):2561–2571

Kaksonen AH, Franzmann PD, Puhakka JA (2003) Performance and ethanol oxidation kinetics of a sulfate-reducing fluidized-bed reactor treating acidic metal-containing wastewater. Biodegradation 14(3):207–217

Kaksonen AH, Plumb JJ, Franzmann PD, Puhakka JA (2004) Simple organic electron donors support diverse sulfate-reducing communities in fluidized-bed reactors treating acidic metal-and sulfate-containing wastewater. FEMS Microbiol Ecol 47(3):279–289

Kaksonen AH, Plumb JJ, Robertson WJ, Riekkola-Vanhanen M, Franzmann PD, Puhakka JA (2006) The performance, kinetics and microbiology of sulfidogenic fluidized-bed treatment of acidic metal-and sulfate-containing wastewater. Hydrometallurgy 83(1–4):204–213

Kefeni KK, Msagati TA, Mamba BB (2017) Acid mine drainage: prevention, treatment options, and resource recovery: a review. J Clean Prod 151:475–493

Keller KL, Wall JD (2011) Genetics and molecular biology of the electron flow for sulfate respiration in Desulfovibrio. Front Microbiol 2:135

Keller KL, Rapp-Giles BJ, Semkiw ES, Porat I, Brown SD, Wall JD (2014) New model for electron flow for sulfate reduction in Desulfovibrio alaskensis G20. Appl Environ Microbiol 80(3):855–868

Khummalai N, Boonamnuayvitaya V (2005) Suppression of arsenopyrite surface oxidation by sol-gel coatings. J Biosci Bioeng 99(3):277–284

Kieu HT, Müller E, Horn H (2011) Heavy metal removal in anaerobic semi-continuous stirred tank reactors by a consortium of sulfate-reducing bacteria. Water Res 45(13):3863–3870

Kimura S, Hallberg KB, Johnson DB (2006) Sulfidogenesis in low pH (3.8–4.2) media by a mixed population of acidophilic bacteria. Biodegradation 17(2):57–65

Kiran MG, Pakshirajan K, Das G (2017) An overview of sulfidogenic biological reactors for the simultaneous treatment of sulfate and heavy metal rich wastewater. Chem Eng Sci 158:606–620

Kleinmann RL, Crerar DA, Pacelli RR (1981) Biogeochemistry of acid mine drainage and a method to control acid formation. Min Eng (NY);(United States) 33(3)

Kobayashi K, Tachibana S, Ishimoto M (1969) Intermediary formation of trithionate in sulfite reduction by a sulfate-reducing bacterium. J Biochem 65:155–157

Kobayashi K, Seki Y, Ishimoto M (1974) Biochemical studies on sulfate-reducing bacteria. XIII. Sulfite reductase from Desulfovibrio vulgaris-mechanism of trithionate, thiosulfate, and sulfite formation and enzymatic properties. J Biochem 75:519–529

Kolmert Å, Johnson DB (2001) Remediation of acidic waste waters using immobilised, acidophilic sulfate-reducing bacteria. J Chem Technol Biotechnol: Int Res Process, Environ Clean Technol 76(8):836–843

Koryak M, Shapiro MA, Sykora JL (1972) Riffle zoobenthos in streams receiving acid mine drainage. Water Res 6(10):1239–1247

Koschorreck M (2008) Microbial sulphate reduction at a low pH. FEMS Microbiol Ecol 64(3):329–342

Krulwich TA, Sachs G, Padan E (2011) Molecular aspects of bacterial pH sensing and homeostasis. Nat Rev Microbiol 9(5):330

Kuyucak N (2002) Acid mine drainage prevention and control options. CIM Bull 95:96–102

Lamrabet O, Pieulle L, Aubert C, Mouhamar F, Stocker P, Dolla A, Brasseur G (2011) Oxygen reduction in the strict anaerobe Desulfovibrio vulgaris Hildenborough: characterization of two membrane-bound oxygen reductases. Microbiology 157(9):2720–2732

Le Pape P, Battaglia-Brunet F, Parmentier M, Joulian C, Gassaud C, Fernandez-Rojo L et al (2017) Complete removal of arsenic and zinc from a heavily contaminated acid mine drainage via an indigenous SRB consortium. J Hazard Mater 321:764–772

Lefticariu L, Walters ER, Pugh CW, Bender KS (2015) Sulfate reducing bioreactor dependence on organic substrates for remediation of coal-generated acid mine drainage: field experiments. Appl Geochem 63:70–82

Leita L, De Nobili M, Muhlbachova G, Mondini C, Marchiol L, Zerbi G (1995) Bioavailability and effects of heavy metals on soil microbial biomass survival during laboratory incubation. Biol Fertil Soils 19(2–3):103–108

Li X, Luo Q, Wofford NQ, Keller KL, McInerney MJ, Wall JD, Krumholz LR (2009) A molybdopterin oxidoreductase is involved in H2 oxidation in Desulfovibrio desulfuricans G20. J Bacteriol 191(8):2675–2682

Liao J, Wen Z, Ru X, Chen J, Wu H, Wei C (2016) Distribution and migration of heavy metals in soil and crops affected by acid mine drainage: public health implications in Guangdong Province, China. Ecotoxicol Environ Saf 124:460–469

Liu Y, Dang Z, Xu Y, Xu T (2013) Pyrite passivation by triethylenetetramine: an electrochemical study. J Anal Methods Chem 2013:387124

Liu Z, Li L, Li Z, Tian X (2018a) Removal of sulfate and heavy metals by sulfate-reducing bacteria in an expanded granular sludge bed reactor. Environ Technol 39(14):1814–1822

Liu F, Qiao X, Zhou L, Zhang J (2018b) Migration and fate of acid mine drainage pollutants in calcareous soil. Int J Environ Res Public Health 15(8):1759

Logan MV, Reardon KF, Figueroa LA, McLain JE, Ahmann DM (2005) Microbial community activities during establishment, performance, and decline of bench-scale passive treatment systems for mine drainage. Water Res 39(18):4537–4551

Lopez-Luna EL (2008) Contributions of iron (III) and sulfate-reducing bacteria to attenuation of an Acid Mine Drainage site: linking microcosm studies and geochemistry. University of Massachusetts Amherst, Amherst

Lottermoser B (2007) Mine wastes. Springer-Verlag, Berlin Heidelberg, pp 43–118

Lu J, Chen T, Wu J, Wilson PC, Hao X, Qian J (2011) Acid tolerance of an acid mine drainage bioremediation system based on biological sulfate reduction. Bioresour Technol 102(22):10401–10406

Manders P, Godfrey L, Hobbs P (2009) Briefing note: acid mine drainage in South Africa. CSIR, Pretoria. http://www.csir.co.za. Accessed 1 Mar 2013

Marsden AD, DeWreede RE (2000) Marine macroalgal community structure, metal content and reproductive function near an acid mine drainage outflow. Environ Pollut 110(3):431–440

Martin AJ, Goldblatt R (2007) Speciation, behavior, and bioavailability of copper downstream of a mine-impacted lake. Environ Toxicol Chem, Int J 26(12):2594–2603

Martins M, Pereira IA (2013) Sulfate-reducing bacteria as new microorganisms for biological hydrogen production. Int J Hydrog Energy 38(28):12294–12301

Martins M, Santos ES, Faleiro ML, Chaves S, Tenreiro R, Barros RJ, Costa MC (2011) Performance and bacterial community shifts during bioremediation of acid mine drainage from two Portuguese mines. Int Biodeterior Biodegradation 65(7):972–981

Martins M, Mourato C, Pereira IA (2015) Desulfovibrio vulgaris growth coupled to formate-driven H2 production. Environ Sci Technol 49(24):14655–14662

McCarthy TS (2011) The impact of acid mine drainage in South Africa. S Afr J Sci 107(5–6):01–07

McCullough CD, Lund MA (2011) Bioremediation of Acidic and Metalliferous Drainage (AMD) through organic carbon amendment by municipal sewage and green waste. J Environ Manag 92(10):2419–2426

McGlynn SE, Chadwick GL, Kempes CP, Orphan VJ (2015) Single cell activity reveals direct electron transfer in methanotrophic consortia. Nature 526(7574):531

Méndez-García C, Peláez AI, Mesa V, Sánchez J, Golyshina OV, Ferrer M (2015) Microbial diversity and metabolic networks in acid mine drainage habitats. Front Microbiol 6:475

Meyer B, Kuehl JV, Price MN, Ray J, Deutschbauer AM, Arkin AP, Stahl DA (2014) The energy-conserving electron transfer system used by D esulfovibrio alaskensis strain G 20 during pyruvate fermentation involves reduction of endogenously formed fumarate and cytoplasmic and membrane-bound complexes, Hdr-Flox and Rnf. Environ Microbiol 16(11):3463–3486

Milucka J, Ferdelman TG, Polerecky L, Franzke D, Wegener G, Schmid M et al (2012) Zero-valent sulphur is a key intermediate in marine methane oxidation. Nature 491(7425):541

Mohanakrishnan J, Gutierrez O, Meyer RL, Yuan Z (2008) Nitrite effectively inhibits sulfide and methane production in a laboratory scale sewer reactor. Water Res 42(14):3961–3971

Monserrate M (2004) Field and column studies of sulfate reducing bacteria in acid mine drainage (Doctoral dissertation, MS Thesis. Department of Civil and Environmental Engineering, University of Massachusetts-Amherst, 100p)

Moosa S, Harrison STL (2006) Product inhibition by sulphide species on biological sulphate reduction for the treatment of acid mine drainage. Hydrometallurgy 83(1–4):214–222

Morais-Silva FO, Santos CI, Rodrigues R, Pereira IA, Rodrigues-Pousada C (2013) Roles of HynAB and Ech, the only two hydrogenases found in the model sulfate reducer Desulfovibrio gigas. J Bacteriol 195(20):4753–4760

Morales TA, Dopson M, Athar R, Herbert RB Jr (2005) Analysis of bacterial diversity in acidic pond water and compost after treatment of artificial acid mine drainage for metal removal. Biotechnol Bioeng 90(5):543–551

Motsi T, Rowson NA, Simmons MJH (2009) Adsorption of heavy metals from acid mine drainage by natural zeolite. Int J Miner Process 92(1–2):42–48

Muhammad SN, Kusin FM, Madzin Z (2018) Coupled physicochemical and bacterial reduction mechanisms for passive remediation of sulfate-and metal-rich acid mine drainage. Int J Environ Sci Technol 15(11):2325–2336

Murray AJ, Roussel J, Rolley J, Woodhall F, Mikheenko IP, Johnson DB et al (2017) Biosynthesis of zinc sulfide quantum dots using waste off-gas from a metal bioremediation process. RSC Adv 7(35):21484–21491

Muyzer G, Stams AJ (2008) The ecology and biotechnology of sulphate-reducing bacteria. Nat Rev Microbiol 6(6):441

Nagase N, Asano S, Takano M, Takeda K, Heguri S, Idegami A (2011) U.S. Patent No. 8,052,774. U.S. Patent and Trademark Office, Washington, DC

Nagpal S, Chuichulcherm S, Peeva L, Livingston A (2000) Microbial sulfate reduction in a liquid–solid fluidized bed reactor. Biotechnol Bioeng 70(4):370–380

Naicker K, Cukrowska E, McCarthy TS (2003) Acid mine drainage arising from gold mining activity in Johannesburg, South Africa and environs. Environ Pollut 122(1):29–40

Ňancucheo I, Johnson DB (2012) Selective removal of transition metals from acidic mine waters by novel consortia of acidophilic sulfidogenic bacteria. Microb Biotechnol 5(1):34–44

Ňancucheo I, Johnson DB (2014) Removal of sulfate from extremely acidic mine waters using low pH sulfidogenic bioreactors. Hydrometallurgy 150:222–226

Nancucheo I, Bitencourt JA, Sahoo PK, Alves JO, Siqueira JO, Oliveira G (2017) Recent developments for remediating acidic mine waters using sulfidogenic bacteria. Biomed Res Int 2017:1–17

Neculita CM, Zagury GJ, Bussière B (2007) Passive treatment of acid mine drainage in bioreactors using sulfate-reducing bacteria. J Environ Qual 36(1):1–16

Neculita CM, Zagury GJ, Bussière B (2008) Effectiveness of sulfate-reducing passive bioreactors for treating highly contaminated acid mine drainage: I. Effect of hydraulic retention time. Appl Geochem 23(12):3442–3451

Neculita CM, Zagury GJ, Kulnieks V (2010) Short-term and long-term bioreactors for acid mine drainage treatment. Proc Annu Int Conf Soils, Sedim, Water Energy 12(1):2

Neculita CM, Yim GJ, Lee G, Ji SW, Jung JW, Park HS, Song H (2011) Comparative effectiveness of mixed organic substrates to mushroom compost for treatment of mine drainage in passive bioreactors. Chemosphere 83(1):76–82

Nielsen G, Janin A, Coudert L, Blais JF, Mercier G (2018) Performance of sulfate-reducing passive bioreactors for the removal of cd and Zn from mine drainage in a cold climate. Mine Water Environ 37(1):42–55

Nieto JM, Sarmiento AM, Olías M, Canovas CR, Riba I, Kalman J, Delvalls TA (2007) Acid mine drainage pollution in the Tinto and Odiel rivers (Iberian Pyrite Belt, SW Spain) and bioavailability of the transported metals to the Huelva Estuary. Environ Int 33(4):445–455

Nordstrom DK (2000) Advances in the hydrogeochemistry and microbiology of acid mine waters. Int Geol Rev 42(6):499–515

Nordstrom DK, Alpers CN (1999) Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California. Proc Natl Acad Sci 96(7):3455–3462

Nyquist J, Greger M (2009) A field study of constructed wetlands for preventing and treating acid mine drainage. Ecol Eng 35(5):630–642

Ochieng GM, Seanego ES, Nkwonta OI (2010) Impacts of mining on water resources in South Africa: a review. Sci Res Essays 5(22):3351–3357

Odom JM, Peck HD Jr (1981) Hydrogen cycling as a general mechanism for energy coupling in the sulfate-reducing bacteria, Desulfovibrio sp. FEMS Microbiol Lett 12(1):47–50

Odom JM, Singleton R (1993) The sulfate-reducing bacteria: contemporary perspectives. Springer-Verlag, New York, pp 189–210

Olıas M, Nieto JM, Sarmiento AM, Cerón JC, Cánovas CR (2004) Seasonal water quality variations in a river affected by acid mine drainage: the Odiel River (South West Spain). Sci Total Environ 333(1–3):267–281

Onysko SJ, Kleinmann RL, Erickson PM (1984) Ferrous iron oxidation by thiobacillus ferrooxidans: inhibition with benzoic acid, sorbic acid, and sodium lauryl sulfate. Appl Environ Microbiol 48(1):229–231

Ozuolmez D, Na H, Lever MA, Kjeldsen KU, Jørgensen BB, Plugge CM (2015) Methanogenic archaea and sulfate reducing bacteria co-cultured on acetate: teamwork or coexistence? Front Microbiol 6:492

Pagnanelli F, Viggi CC, Mainelli S, Toro L (2009) Assessment of solid reactive mixtures for the development of biological permeable reactive barriers. J Hazard Mater 170(2–3):998–1005

Pandey PK, Sharma R, Roy M, Pandey M (2007) Toxic mine drainage from Asia's biggest copper mine at Malanjkhand, India. Environ Geochem Health 29(3):237–248

Pandey S, Yacob TW, Silverstein J, Rajaram H, Minchow K, Basta J (2011) Prevention of acid mine drainage through complexation of ferric iron by soluble microbial growth products. In: AGU Fall Meeting Abstracts

Park I, Tabelin CB, Jeon S, Li X, Seno K, Ito M, Hiroyoshi N (2018) A review of recent strategies for acid mine drainage prevention and mine tailings recycling. Chemosphere 219:588–606

Pat-Espadas A, Loredo Portales R, Amabilis-Sosa L, Gómez G, Vidal G (2018) Review of constructed wetlands for acid mine drainage treatment. Water 10(11):1685

Paulo LM, Stams AJ, Sousa DZ (2015) Methanogens, sulphate and heavy metals: a complex system. Rev Environ Sci Biotechnol 14(4):537–553

Peck HD, LeGall J (1982) Biochemistry of dissimilatory sulphate reduction. Philos Trans R Soc Lond B Biol Sci 298(1093):443–466

Peltier E, Ilipilla P, Fowle D (2011) Structure and reactivity of zinc sulfide precipitates formed in the presence of sulfate-reducing bacteria. Appl Geochem 26(9–10):1673–1680

Pereira IA, Romão CV, Xavier AV, LeGall J, Teixeira M (1998) Electron transfer between hydrogenases and mono-and multiheme cytochromes in Desulfovibrio ssp. JBIC J Biol Inorganic Chem 3(5):494–498

Pereira PM, Teixeira M, Xavier AV, Louro RO, Pereira IA (2006) The Tmc complex from Desulfovibrio vulgaris Hildenborough is involved in transmembrane electron transfer from periplasmic hydrogen oxidation. Biochemistry 45(34):10359–10367

Pereira IA, Ramos AR, Grein F, Marques MC, Da Silva SM, Venceslau SS (2011) A comparative genomic analysis of energy metabolism in sulfate reducing bacteria and archaea. Front Microbiol 2:69

Pereyra LP, Hiibel SR, Perrault EM, Reardon KF, Pruden A (2012) Effect of bioaugmentation and biostimulation on sulfate-reducing column startup captured by functional gene profiling. FEMS Microbiol Ecol 82(1):135–147

Pérez N, Schwarz AO, Barahona E, Sanhueza P, Diaz I, Urrutia H (2018) Performance of two differently designed permeable reactive barriers with sulfate and zinc solutions. Sci Total Environ 642:894–903

Pérez-Ostalé E, Grande JA, de la Torre ML, Valente T, Cerón JC, Santisteban M (2013) Inventory of mining and quantification of affected areas in the iberian pyrite belt (SW Spain). A methodological contribution to environmental management. Int Multidisciplin Sci GeoConf: SGEM: Surv Geol Mining Ecol Manag 1:613

Picard A, Gartman A, Clarke DR, Girguis PR (2018) Sulfate-reducing bacteria influence the nucleation and growth of mackinawite and greigite. Geochim Cosmochim Acta 220:367–384

Plugge CM, Zhang W, Scholten J, Stams AJ (2011) Metabolic flexibility of sulfate-reducing bacteria. Front Microbiol 2:81

Potgieter-Vermaak SS, Potgieter JH, Monama P, Van Grieken R (2006) Comparison of limestone, dolomite and fly ash as pre-treatment agents for acid mine drainage. Miner Eng 19(5):454–462

Price MN, Ray J, Wetmore KM, Kuehl JV, Bauer S, Deutschbauer AM, Arkin AP (2014) The genetic basis of energy conservation in the sulfate-reducing bacterium Desulfovibrio alaskensis G20. Front Microbiol 5:577

Pruden A, Messner N, Pereyra L, Hanson RE, Hiibel SR, Reardon KF (2007) The effect of inoculum on the performance of sulfate-reducing columns treating heavy metal contaminated water. Water Res 41(4):904–914

Qian Z, Tianwei H, Mackey HR, van Loosdrecht MC, Guanghao C (2018) Recent advances in dissimilatory sulfate reduction: from metabolic study to application. Water Res 150:162–181

Qiu G, Feng X, Wang S, Fu X, Shang L (2009) Mercury distribution and speciation in water and fish from abandoned Hg mines in Wanshan, Guizhou province, China. Sci Total Environ 407(18):5162–5168

Quintas PO, Oliveira MS, Catarino T, Turner DL (2013) Electron transfer between multihaem cytochromes c3 from Desulfovibrio africanus. Biochim Biophys Acta (BBA)-Bioenerg 1827(4):502–506

Rabus R, Hansen TA, Widdel F (2006) Dissimilatory sulfate- and sulfur-reducing prokaryotes. In: Dworkin M, Falkow S, Rosenberg E, Schleifer KH, Stackebrandt E (eds) The prokaryotes, Ecophysiology and biochemistry, vol 2. Springer, Berlin, pp 659–768

Rabus R, Hansen TA, Widdel F (2013) Dissimilatory sulfate-and sulfur-reducing prokaryotes. In: The prokaryotes: prokaryotic physiology and biochemistry. Springer-Verlag, Berlin Heidelberg, pp 309–404

Ramos AR, Keller KL, Wall JD, Pereira IAC (2012) The membrane QmoABC complex interacts directly with the dissimilatory adenosine 5-phosphosulfate reductase in sulfate reducing bacteria. Front Microbiol 3:137

Raskin L, Rittmann BE, Stahl DA (1996) Competition and coexistence of sulfate-reducing and methanogenic populations in anaerobic biofilms. Appl Environ Microbiol 62(10):3847–3857

Reid NB, Naeth MA (2005) Establishment of a vegetation cover on tundra kimberlite mine tailings: 2. A field study. Restorat Ecol 13(4):602–608

Reis MAM, Lemos PC, Almeida JS, Carrondo MJT (1990) Influence of produced acetic acid on growth of sulfate reducing bacteria. Biotechnol Lett 12(2):145–148

Reis MAM, Almeida JS, Lemos PC, Carrondo MJT (1992) Effect of hydrogen sulfide on growth of sulfate reducing bacteria. Biotechnol Bioeng 40(5):593–600

Riekkola-Vanhanen M, Mustikkamäki UP (1997) In situ treatment of acid mine drainage by sulphate reducing bacteria in an open pit mine. In: Proceedings of biomine international conference, Sydney, Australia, pp E-ROM3.1-E-ROM3.8

Rodríguez-Galán M, Baena-Moreno FM, Vázquez S, Arroyo-Torralvo F, Vilches LF, Zhang Z (2019) Remediation of acid mine drainage. Environ Chem Lett 2019:1–10

RoyChowdhury A, Sarkar D, Datta R (2015) Remediation of acid mine drainage-impacted water. Curr Pollut Rep 1(3):131–141

RoyChowdhury A, Sarkar D, Deng Y, Datta R (2017) Assessment of soil and water contamination at the tab-simco coal mine: a case study. Mine Water Environ 36(2):248–254

RoyChowdhury A, Sarkar D, Datta R (2019) Removal of acidity and metals from acid mine drainage-impacted water using industrial byproducts. Environ Manag 63(1):148–158

Rubio-Rincón F, Lopez-Vazquez C, Welles L, van den Brand T, Abbas B, van Loosdrecht M, Brdjanovic D (2017) Effects of electron acceptors on sulphate reduction activity in activated sludge processes. Appl Microbiol Biotechnol 101(15):6229–6240

Saha S, Sinha A (2018) A review on treatment of acid mine drainage with waste materials: a novel approach. Global NEST J 20(3):512–528

Sahinkaya E, Yurtsever A, Toker Y, Elcik H, Cakmaci M, Kaksonen AH (2015) Biotreatment of As-containing simulated acid mine drainage using laboratory scale sulfate reducing upflow anaerobic sludge blanket reactor. Miner Eng 75:133–139

Sahoo PK, Tripathy S, Equeenuddin SM, Panigrahi MK (2012) Geochemical characteristics of coal mine discharge vis-à-vis behavior of rare earth elements at Jaintia Hills coalfield, northeastern India. J Geochem Explor 112:235–243

Sahoo PK, Kim K, Equeenuddin SM, Powell MA (2013) Current approaches for mitigating acid mine drainage. In: Reviews of environmental contamination and toxicology, vol 226. Springer, New York, pp 1–32

Sánchez-Andrea I, Triana D, Sanz JL (2012) Bioremediation of acid mine drainage coupled with domestic wastewater treatment. Water Sci Technol 66(11):2425–2431

Sánchez-Andrea I, Sanz JL, Bijmans MF, Stams AJ (2014) Sulfate reduction at low pH to remediate acid mine drainage. J Hazard Mater 269:98–109

Sani RK, Peyton BM, Brown LT (2001) Copper-induced inhibition of growth of Desulfovibrio desulfuricans G20: assessment of its toxicity and correlation with those of zinc and lead. Appl Environ Microbiol 67(10):4765–4772

Sani RK, Peyton BM, Jandhyala M (2003) Toxicity of lead in aqueous medium to Desulfovibrio desulfuricans G20. Environ Toxicol Chem 22(2):252–260

Santos AL, Johnson DB (2017) The effects of temperature and pH on the kinetics of an acidophilic sulfidogenic bioreactor and indigenous microbial communities. Hydrometallurgy 168:116–120

Santos AA, Venceslau SS, Grein F, Leavitt WD, Dahl C, Johnston DT, Pereira IA (2015) A protein trisulfide couples dissimilatory sulfate reduction to energy conservation. Science 350(6267):1541–1545

Sato Y, Hamai T, Hori T, Habe H, Kobayashi M, Sakata T (2018) Year-round performance of a passive sulfate-reducing bioreactor that uses rice bran as an organic carbon source to treat acid mine drainage. Mine Water Environ 37(3):586–594

Scheller S, Yu H, Chadwick GL, McGlynn SE, Orphan VJ (2016) Artificial electron acceptors decouple archaeal methane oxidation from sulfate reduction. Science 351(6274):703–707

Schmidt TS, Soucek DJ, Cherry DS (2002) Modification of an ecotoxicological rating to bioassess small acid mine drainage-impacted watersheds exclusive of benthic macroinvertebrate analysis. Environ Toxicol Chem Int J 21(5):1091–1097

Schmidtova J, Baldwin SA (2011) Correlation of bacterial communities supported by different organic materials with sulfate reduction in metal-rich landfill leachate. Water Res 45(3):1115–1128

Schueck JH, Helfrich DR, Fromell DJ (2004) Limestone upflow pond with siphon discharge design considerations: a simple solution to high volume, high metals AMD discharges. In: Proceedings of the 6th statewide conference on abandoned mine reclamation, Indiana, PA298

Shabalala AN, Ekolu SO, Diop S (2014) Permeable reactive barriers for acid mine drainage treatment: a review. https://doi.org/10.3233/978-1-61499-466-4-1416

Shahid M, Khalid S, Abbas G, Shahid N, Nadeem M, Sabir M et al (2015) Heavy metal stress and crop productivity. In: Crop production and global environmental issues. Springer, Cham, pp 1–25

Shelp G, Chesworth W, Spiers G, Liu L (1995) Cathodic protection of a weathering orebody. In: Proceedings of Sudbury '95—mining and the environment, pp 1035–1042

Sheoran AS (2017) Management of acidic mine waste water by constructed wetland treatment systems: a bench scale study. Eur J Sustain Dev 6(2):245–255

Sheoran AS, Sheoran V (2006) Heavy metal removal mechanism of acid mine drainage in wetlands: a critical review. Miner Eng 19(2):105–116

Shu WS (2003) Exploring the potential utilization of vetiver in treating acid mine drainage (AMD). In: Proceedings of the third international vetiver conference, Guangzhou, China

Shu X, Dang Z, Zhang Q, Yi X, Lu G, Guo C, Yang C (2013) Passivation of metal-sulfide tailings by covalent coating. Miner Eng 42:36–42

Sim MS, Wang DT, Zane GM, Wall JD, Bosak T, Ono S (2013) Fractionation of sulfur isotopes by Desulfovibrio vulgaris mutants lacking hydrogenases or type I tetraheme cytochrome c3. Front Microbiol 4:171

Sim MS, Paris G, Adkins JF, Orphan VJ, Sessions AL (2017) Quantification and isotopic analysis of intracellular sulfur metabolites in the dissimilatory sulfate reduction pathway. Geochim Cosmochim Acta 206:57–72

Simmons J, Ziemkiewicz P, Black D (2002a) Use of steel slag leach beds for the treatment of acid mine drainage: the McCarty Highwall Project. In: Proceedings of the 19th ASMR Conference, Lexington, KY, pp 527–529

Simmons J, Ziemkiewicz P, Black DC (2002b) Use of steel slag leach beds for the treatment of acid mine drainage. Mine Water Environ 21(2):91–99

Skennerton CT, Chourey K, Iyer R, Hettich RL, Tyson GW, Orphan VJ (2017) Methane-fueled syntrophy through extracellular electron transfer: uncovering the genomic traits conserved within diverse bacterial partners of anaerobic methanotrophic archaea. MBio 8(4):e00530–e00517

Skousen J, Zipper CE, Rose A, Ziemkiewicz PF, Nairn R, McDonald LM, Kleinmann RL (2017) Review of passive systems for acid mine drainage treatment. Mine Water Environ 36(1):133–153

Slaninova A, Machova J, Svobodova Z (2014) Fish kill caused by aluminium and iron contamination in a natural pond used for fish rearing: a case report. Veterinarni Med 59(11):573–581

Song YC, Piak BC, Shin HS, La SJ (1998) Influence of electron donor and toxic materials on the activity of sulfate-reducing bacteria for the treatment of electroplating wastewater. Water Sci Tech 38:187–194

Song H, Yim GJ, Ji SW, Neculita CM, Hwang T (2012) Pilot-scale passive bioreactors for the treatment of acid mine drainage: efficiency of mushroom compost vs. mixed substrates for metal removal. J Environ Manag 111:150–158

Soucek DJ, Cherry DS, Trent GC (2000) Relative acute toxicity of acid mine drainage water column and sediments to Daphnia magna in the Puckett's creek watershed, Virginia, USA. Arch Environ Contam Toxicol 38(3):305–310

Stahl DA, Fishbain S, Klein M, Baker BJ, Wagner M (2002) Origins and diversification of sulfate-respiring microorganisms. Antonie Van Leeuwenhoek 81(1–4):189

Stams AJ, Plugge CM (2009) Electron transfer in syntrophic communities of anaerobic bacteria and archaea. Nat Rev Microbiol 7(8):568

Sun M, Xiao T, Ning Z, Xiao E, Sun W (2015) Microbial community analysis in rice paddy soils irrigated by acid mine drainage contaminated water. Appl Microbiol Biotechnol 99(6):2911–2922

Suzuki D, Ueki A, Amaishi A, Ueki K (2007) Desulfobulbus japonicus sp. nov., a novel Gram-negative propionate-oxidizing, sulfate-reducing bacterium isolated from an estuarine sediment in Japan. Int J Syst Evol Microbiol 57(4):849–855

Tamás J, Kovács E (2005) Vegetation pattern and heavy metal accumulation at a mine tailing at Gyöngyösoroszi, Hungary. Zeitschrift für Naturforschung C 60(3–4):362–368

Taylor J, Pape S, Murphy N (2005) A summary of passive and active treatment technologies for acid and metalliferous drainage (AMD). In: Proceedings of the in fifth Australian workshop on acid mine drainage

Teng W, Kuang J, Luo Z, Shu W (2017) Microbial diversity and community assembly across environmental gradients in acid mine drainage. Fortschr Mineral 7(6):106

Thauer RK, Stackebrandt E, Hamilton WA (2007) Energy metabolism and phylogenetic diversity of sulphate-reducing bacteria. Sulphate-reducing bacteria: environmental and engineered systems. Cambridge University Press, Cambridge, pp 1–37

Timms GP, Bennett JW (2000) The effectiveness of covers at Rum Jungle after fifteen years. In: Proceedings fifth international conference on acid rock drainage, pp 813–818

Tiwary RK (2001) Environmental impact of coal mining on water regime and its management. Water Air Soil Pollut 132(1–2):185–199

Trumm D (2010) Selection of active and passive treatment systems for AMD—flow charts for New Zealand conditions. N Z J Geol Geophys 53(2–3):195–210

Tyagi M, da Fonseca MMR, de Carvalho CCCR (2011) Bioaugmentation and biostimulation strategies to improve the effectiveness of bioremediation processes. Biodegradation 22(2):231–241

Utgikar VP, Harmon SM, Chaudhary N, Tabak HH, Govind R, Haines JR (2002) Inhibition of sulfate-reducing bacteria by metal sulfide formation in bioremediation of acid mine drainage. Environ Toxicol Int J 17(1):40–48

Valente T, Gomes P, Pamplona J, de la Torre ML (2012) Natural stabilization of mine waste-dumps—evolution of the vegetation cover in distinctive geochemical and mineralogical environments. J Geochem Explor 123:152–161

Van Damme PA, Hamel C, Ayala A, Bervoets L (2008) Macroinvertebrate community response to acid mine drainage in rivers of the High Andes (Bolivia). Environ Pollut 156(3):1061–1068

Vasquez Y, Escobar MC, Neculita CM, Arbeli Z, Roldan F (2016a) Biochemical passive reactors for treatment of acid mine drainage: effect of hydraulic retention time on changes in efficiency, composition of reactive mixture, and microbial activity. Chemosphere 153:244–253

Vasquez Y, Escobar MC, Neculita CM, Arbeli Z, Roldan F (2016b) Selection of reactive mixture for biochemical passive treatment of acid mine drainage. Environ Earth Sci 75(7):576

Vasquez Y, Escobar MC, Saenz JS, Quiceno-Vallejo MF, Neculita CM, Arbeli Z, Roldan F (2018) Effect of hydraulic retention time on microbial community in biochemical passive reactors during treatment of acid mine drainage. Bioresour Technol 247:624–632

Venceslau SS, Lino RR, Pereira IA (2010) The Qrc membrane complex, related to the alternative complex III, is a menaquinone reductase involved in sulfate respiration. J Biol Chem 285(30):22774–22783

Vestola E (2004) Treatment of acid mine drainage by sulphate reducing bacteria. Master's Thesis, Helsinki University of Technology, Helsinki, Finland [in Finnish]

Wagner M, Loy A, Klein M, Lee N, Ramsing NB, Stahl DA, Friedrich MW (2005) Functional marker genes for identification of sulfate-reducing prokaryotes. Methods Enzymol 397:469–489

Walton WE, Compton SM, Allan JD, Daniels RE (1982) The effect of acid stress on survivorship and reproduction of Daphnia pulex (Crustacea: Cladocera). Can J Zool 60(4):573–579

Wang L, Ji B, Hu Y, Liu R, Sun W (2017) A review on in situ phytoremediation of mine tailings. Chemosphere 184:594–600

Waybrant KR, Blowes DW, Ptacek CJ (1998) Selection of reactive mixtures for use in permeable reactive walls for treatment of mine drainage. Environ Sci Technol 32(13):1972–1979

Wegener G, Krukenberg V, Riedel D, Tegetmeyer HE, Boetius A (2015) Intercellular wiring enables electron transfer between methanotrophic archaea and bacteria. Nature 526(7574):587

Wendt-Potthoff K, Bozau E, Frömmichen R, Meier J, Koschorreck M (2010) Microbial iron reduction during passive in situ remediation of an acidic mine pit lake mesocosm. Limnologica-Ecol Manag Inland Waters 40(2):175–181

Widdel F, Pfennig N (1982) Studies on dissimilatory sulfate-reducing bacteria that decompose fatty acids II. Incomplete oxidation of propionate by Desulfobulbus propionicus gen. nov., sp. nov. Arch Microbiol 131(4):360–365

Xiao KQ, Beulig F, Kjeldsen KU, Jørgensen BB, Risgaard-Petersen N (2017) Concurrent methane production and oxidation in surface sediment from Aarhus Bay, Denmark. Front Microbiol 8:1198

Xingyu L, Zou G, Wang X, Zou L, Wen J, Ruan R, Wang D (2013) A novel low pH sulfidogenic bioreactor using activated sludge as carbon source to treat acid mine drainage (AMD) and recovery metal sulfides: pilot scale study. Miner Eng 48:51–55

Yanful EK, Orlandea MP (2000) Controlling acid drainage in a pyritic mine waste rock. Part II: geochemistry of drainage. Water Air Soil Pollut 124(3–4):259–283

Yanful EK, Payant SC (1992) Evaluation of techniques for preventing acidic rock drainage. Milestone research report, MEND program, December

Yu L, Duan J, Zhao W, Huang Y, Hou B (2011) Characteristics of hydrogen evolution and oxidation catalyzed by Desulfovibrio caledoniensis biofilm on pyrolytic graphite electrode. Electrochim Acta 56(25):9041–9047

Zagury GJ, Kulnieks VI, Neculita CM (2006) Characterization and reactivity assessment of organic substrates for sulphate-reducing bacteria in acid mine drainage treatment. Chemosphere 64(6):944–954

Zagury GJ, Neculita C, Bussiere B (2007) Passive treatment of acid mine drainage in bioreactors: short review, applications, and research needs. In: Proceedings of the 60th Canadian geotechnical conference and 8th joint CGS/IAH-CNC specialty groundwater conference, Ottawa, Canada, pp 1439–1446

Zhang YL, Evangelou VP (1998) Formation of ferric hydroxide-silica coatings on pyrite and its oxidation behavior. Soil Sci 163:53–62

Zhang M, Wang H (2016) Preparation of immobilized sulfate reducing bacteria (SRB) granules for effective bioremediation of acid mine drainage and bacterial community analysis. Miner Eng 92:63–71

Zhang X, Borda MJ, Schoonen MA, Strongin DR (2003a) Adsorption of phospholipids on pyrite and their effect on surface oxidation. Langmuir 19(21):8787–8792

Zhang X, Borda MJ, Schoonen MA, Strongin DR (2003b) Pyrite oxidation inhibition by a cross-linked lipid coating. Geochem Trans 4(1):8

Zhang M, Wang H, Han X (2016) Preparation of metal-resistant immobilized sulfate reducing bacteria beads for acid mine drainage treatment. Chemosphere 154:215–223

Zhang M, Liu X, Li Y, Wang G, Wang Z, Wen J (2017) Microbial community and metabolic pathway succession driven by changed nutrient inputs in tailings: effects of different nutrients on tailing remediation. Sci Rep 7(1):474

Zhong CM, Xu ZL, Fang XH, Cheng L (2007) Treatment of acid mine drainage (AMD) by ultra-low-pressure reverse osmosis and nanofiltration. Environ Eng Sci 24(9):1297–1306

Zhou C, Vannela R, Hayes KF, Rittmann BE (2014) Effect of growth conditions on microbial activity and iron-sulfide production by Desulfovibrio vulgaris. J Hazard Mater 272:28–35

Ziemkiewicz PF, Brant DL (1996) The Casselman river restoration project. In: Proceedings, eighteenth west Virginia surface mine drainage task force symposium, pp 15–16

Ziemkiewicz P, Skousen J (1998) The use of steel slag in acid mine drainage treatment and control. Green Lands 28(1):46–56

Ziemkiewicz PF, Skousen JG, Brant DL, Sterner PL, Lovett RJ (1997) Acid mine drainage treatment with armored limestone in open limestone channels. J Environ Qual 26(4):1017–1024

Ziemkiewicz PF, Skousen JG, Simmons J (2003) Long-term performance of passive acid mine drainage treatment systems. Mine Water Environ 22(3):118–129

Elaboration and Characterization of Porous Materials from Moroccan Natural Resources: Application to Industrial Wastewater Treatment

9

A. Abourriche, M. Oumam, M. Mouiya, S. Mansouri, A. Benhammou, Y. El Hafiane, Y. Abouliatim, L. Nibou, A. Smith, and H. Hannache

Abstract

Within the Moroccan natural resources valorization scheme, new porous materials have been prepared from clay minerals and oil shale. The activation process of the oil shale that we have developed in this study give effective adsorbent materials. In view of their physicochemical characterization and application in the treatment of water loaded with metal (Cr^{6+} ion) or organic (methylene blue) pollutant, we conclude that the chemical activation process at low temperature (250 °C) of the oil shale gives the best material with a high porous structure, which give it a high retention of methylene blue and Cr^{6+} ion. In addition, the ceramic membrane prepared in this study by mixing raw clay and oil shale could be a perfect candidate for prepurification of strongly alkaline industrial waste liquids, as for pretreatment of seawater desalination because of its low cost, easy fabrication, and high turbidity removal efficiency.

A. Abourriche (✉) · M. Mouiya
Laboratory of Materials, Processes, Environment and Quality, National Schools of Applied Sciences of Safi, University of Cadi Ayyad, Safi, Morocco

Laboratory of Thermostructural Materials, Faculty of Sciences Ben M'sik, University of Hassan II, Casablanca, Morocco
e-mail: a.abourriche@uca.ma

M. Oumam · S. Mansouri · H. Hannache
Laboratory of Thermostructural Materials, Faculty of Sciences Ben M'sik, University of Hassan II, Casablanca, Morocco

A. Benhammou · Y. Abouliatim · L. Nibou
Laboratory of Materials, Processes, Environment and Quality, National Schools of Applied Sciences of Safi, University of Cadi Ayyad, Safi, Morocco

Y. El Hafiane · A. Smith
Institute of Research on Ceramics (IRCER), UMR CNRS 7315, Limoges Cedex, France

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_9

Keywords
Clay · Oil Shale · Porous Ceramic · Adsorbents · Industrial wastewater

9.1 Introduction

Environmental protection has become a critical social issue, and its consideration by all enterprises is necessary for legal and economic reasons. Some of the critical environmental issues are water pollution, industrial emissions of toxic substances, mercury and other toxic heavy metals, and oil in the oceans. Therefore, the development of effective effluent treatment methods is a matter of great practical importance (Le and Nunes 2016).

Membrane technology (e.g., microfiltration (MF), ultrafiltration, or nanofiltration) is considered an effective means of effluent purification (Khemakhem et al. 2017a), which accounts for the broad variety of employed separation membranes. In particular, ceramic membranes are widely studied owing to their excellent mechanical properties, thermal stability, good chemical resistance, and long lifetime, and a number of ceramic membranes for industrial separation applications are already commercially available (Jeong et al. 2017).

Ceramic membranes comprise a membrane layer and a porous ceramic support (based on structures such as fibers, foams, interconnected rods, hollow spheres, or honeycombs (Ohji and Fukushima 2012)) and can be produced by compaction processes, sol-gel methods (Samain et al. 2014), and extrusion (Fan et al. 2016) and hydrothermal synthesis (Wang et al. 2012) techniques. Among these techniques, compaction is the one most frequently used method for fabricating porous ceramics (Mouiya et al. 2017; Stawiskia 2014) and relies on the incorporation of a sacrificial phase (known as a pore-forming agent or porogen) into the starting mixture for pore generation. Such ceramic supports provide sufficient strength as well as a highly porous texture (Dabir et al. 2017) and hence allow effluent filtration at high flux rates, producing filtrates with low turbidity levels; therefore, they are effective filter media for processes such as drinking water production and effluent pretreatment (Achiou et al. 2017; Mouiya et al. 2018a).

Otherwise, activated carbon is an efficient adsorbent for the remediation of wastewaters. Therefore, researches have focused on the development of activated carbons from industrial or agricultural wastes such as apricot stones (Moreno-Castilla et al. 2001; Molina-Sabio et al. 1995), sawdust (Benaddi et al. 2000), bagasse (Valix et al. 2004; Castro et al. 2000a), globe artichoke leaves (Benadjemia et al. 2011), bark of pomegranate (Bestani et al. 2008), molasses (Legrouri et al. 2005), or nut shells (Jaguaribe et al. 2005). Different activation methods are used in order to achieve a material with adsorbing properties.

Within this context, we have carried out researches to explore the opportunity of producing porous materials from Moroccan abundant natural resources, that is, clays and oil shales, in order to find new applications of the Moroccan oil shales. More specifically, we aimed to demonstrate that the ceramic membrane prepared in this study by mixing raw clay and oil shale could be a perfect candidate for prepurification of strongly alkaline industrial waste liquids, as for pretreatment of seawater desalination because of its low cost, easy fabrication and high turbidity removal efficiency.

9.2 New Adsorbent Materials Obtained from Moroccan Oil Shale

This section gives an overview on the preparation of the adsorbent materials from Moroccan oil shale. The oil shale used in this work was from the Tarfaya deposit located in the South of Morocco. This deposit consists of several layers that are in turn subdivided in sub-layers, each having a different amount of organic matter. The samples were obtained from the so-called $\mathbf{R_3}$ sub-layer characterized by its high content of organic matter (Cavalier and Chornet 1978). Its chemical composition is given in Table 9.1 **(**Bekri and Ziyad 1991).

9.2.1 Preparation of the Raw Material

The carbonate-free oil shale was obtained by dissolution of carbonates with HCl (Abourriche et al. 2003; Yürüm et al. 1985). The powdered $\mathbf{R_3}$ shale (20 g, grain size 0.063–0.08 mm) and 80 mL of concentrated HCl (7 M) were introduced in an Erlenmeyer. The mixture was then subjected to magnetic stirring for 4 h. The formed CO_2 was trapped by bubbling in a solution of barium hydroxide. After filtration, the solid residue (referred to as RH) was washed carefully with distilled water, dried at 100 °C, and stocked in a sealed plastic bag.

9.2.2 Characterization of RH

Comparing the results of Electron spectroscopy for chemical analysis (ESCA) (Table 9.2) reveals that RH is characterized by the absence of Ca and Mg, which shows that the attack on the rough rock R_3 by hydrochloric acid allowed dissolving completely the carbonate. These results were confirmed by Electron Probe Microanalysis (EPMA) (Fig. 9.1). Moreover, EPMA revealed the presence of other elements at greater depths that could not be detected by X-ray photoelectron spectroscopy (XPS).

Table 9.1 The general characteristics of the R_3 sub-layer

Composition	wt %
Carbonates	70.0
Kerogen	20.0
Silicates	7.1
Pyrite	1.0
Bitumen	0.9
Moisture	17.5
Ashes	54.9
Volatile	40.2
Organic carbon	11.3

Table 9.2 XPS analyses of the starting materials (atomic %)

Element	R_3	RH
Fe (2p3)	0.2	0.1
O (1 s)	36.5	26.9
N (1 s)	0.4	1.3
C (1 s)	43.4	56.0
Cl (2p)	2.5	0.4
S (2p)	0.8	2.1
Al (2 s)	2.4	3.7
Si (2p)	3.2	8.2
Ca (2p)	9.3	–
Mg	0.1	–
Na	0.2	–

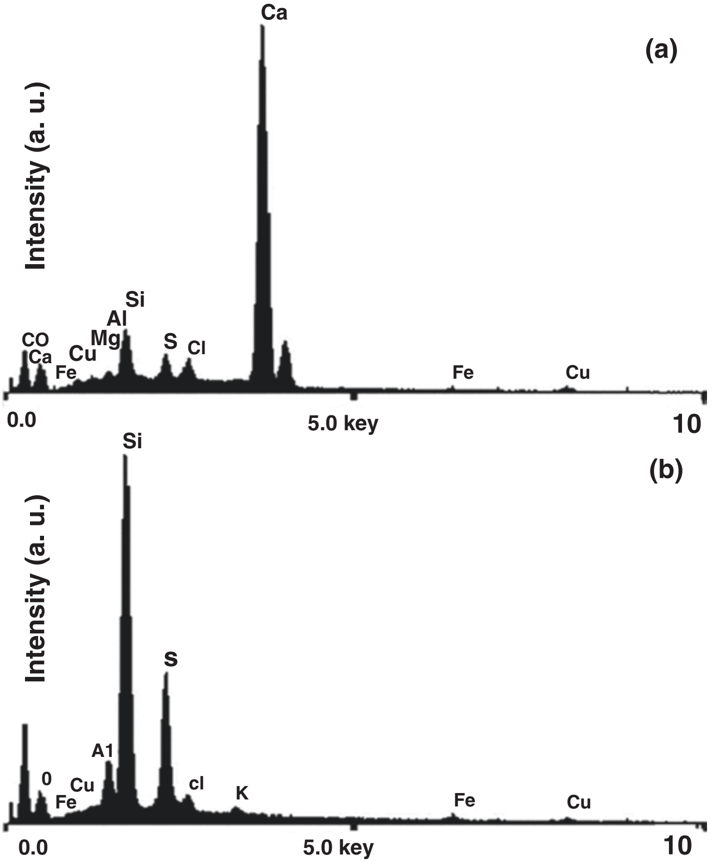


Fig. 9.1 Energy dispersive X-ray (EDX) spectra of the samples (**a**) R_3 and (**b**) RH

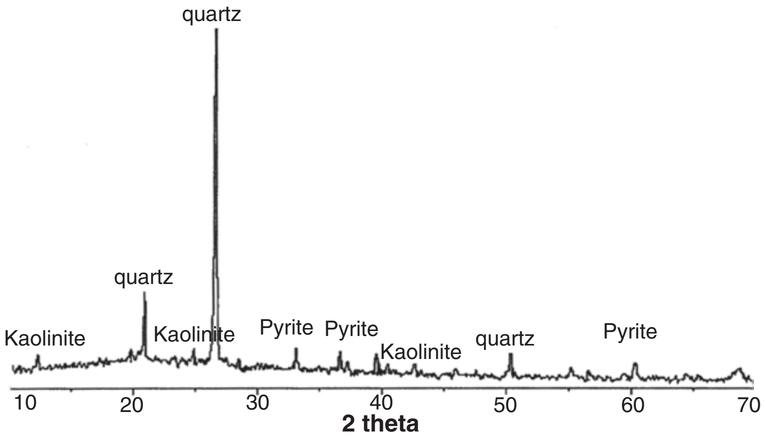


Fig. 9.2 X-ray diffraction (XRD) of the sample RH

Analysis of the diffraction pattern RX shown in Fig. 9.2 shows that the RH mineral matrix consists essentially of quartz. Pyrite and kaolinite are also present in small quantities compared to quartz. The SEM analysis of RH shows that it is a microporous material, on which there is a uniform distribution of grain size which is of the order of 1 μm. The resulting value S_{BET} is of the order of 13 $\mathrm{m}^2\ \mathrm{g}^{-1}$.

The results of thermogravimetric analyzes (TGA/DTA) (Fig. 9.3) show that RH is characterized by a continuous mass loss ranging from about 150 °C to 535 °C, reflecting the elimination of groups and chains resulting from the degradation of organic matter by air oxidation. This oxidation results on the DTA curve in an exothermic peak with a maximum set at 260 °C. The DTA curve displays also an endothermic peak whose maximum is situated around 480 °C. This peak can be due to processing of organic carbon, or oxidation or decomposition of the mineral matter present in RH.

9.2.3 Variation the Yield of Adsorbents Materials Obtained at Different Temperatures

We determined the yield R of the obtained materials by the following formula:

$$R = \frac{m_f}{m_i} \times 100$$

where m_{i} is the mass of RH initially introduced into the furnace and m_{f} the mass of adsorbent materials prepared.

The histogram in Fig. 9.4 gives the evolution of the yields of adsorbent materials obtained at different temperatures. Low value yields result from severe oxidation of the organic matter of RH by oxygen in air. This promotes the complete degradation

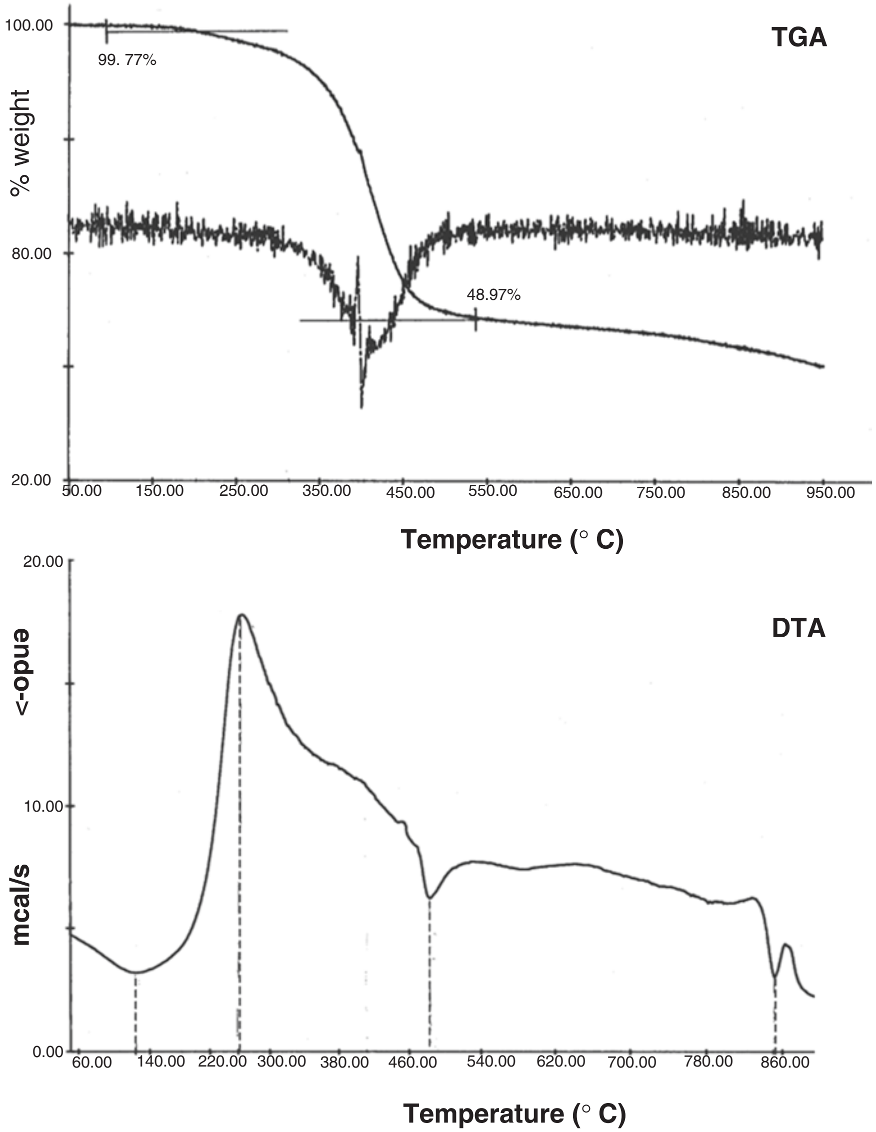


Fig. 9.3 Thermal curves of the sample RH

of the kerogen even at low temperature, to end at 550 °C with ash completely devoid of organic matter. The amount of ash at 550 °C of 22% shows that RH was composed of about 78% organic matter and 22% mineral matter.

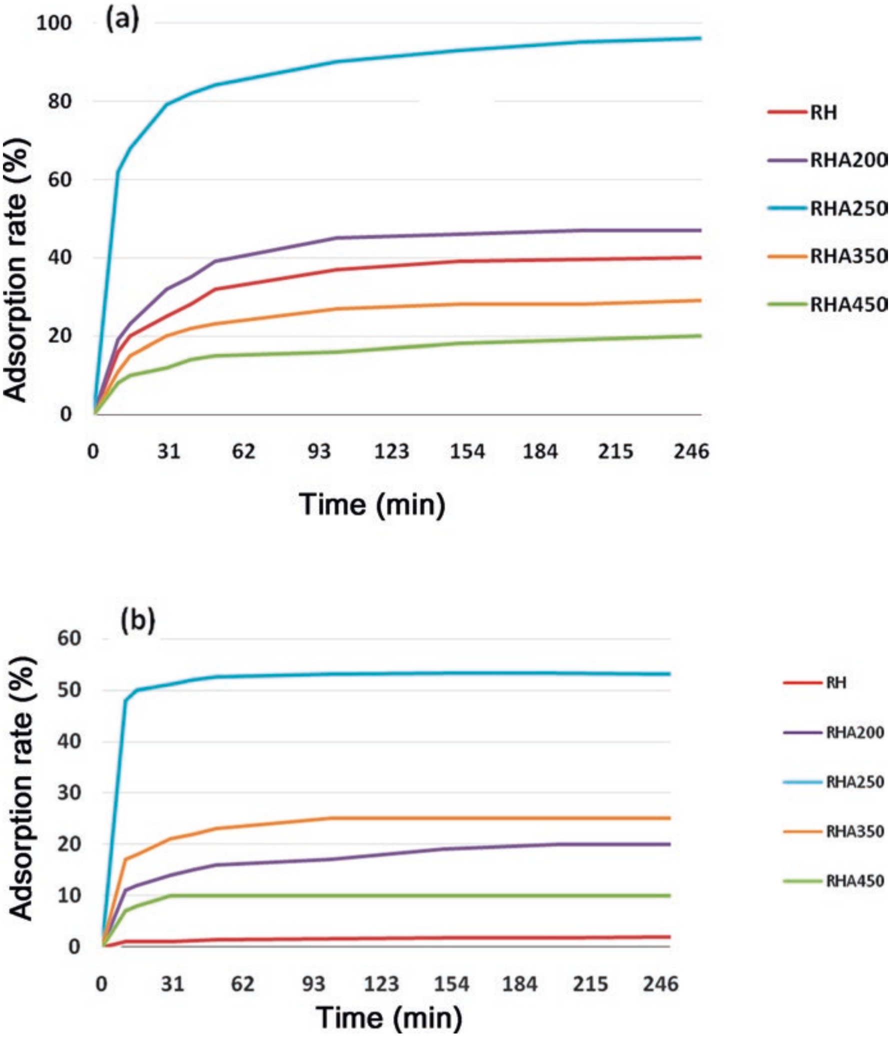


Fig. 9.4 Adsorption kinetics of (**a**) methylene blue and (**b**) Cr^{6+} ion onto RHA adsorbents obtained by physical activation

9.2.4 Preparation of the Adsorbents by Physical Activation

The thermal process was based on the calcination of RH in air at different temperatures. Processing temperatures were 200, 250, 350, and 450 °C. The materials obtained after heat treatment will be labelled RHA200, RHA250, RHA350, and RHA450.

Table 9.3 Effect of the activation temperature on the adsorption capacity of adsorbents obtained by physical activation

Sample	Adsorption capacity (mg/g)	
	Methylene blue	Cr^{6+} ion
RH	15.4	1.5
RHA200	17.2	5.1
RHA250	37.0	8.4
RHA350	10.1	6.4
RHA450	6.8	5.4

9.2.5 Effect of Activation Temperature on the Adsorption Capacity

The curves in Fig. 9.4 show the evolution of the adsorption performances of RHA samples as a function of time. In the case of Methylene bleu (MB) (Fig. 9.4a) the saturation of the different samples was reached after almost 2 h of contact between the adsorbent and the adsorbate. The adsorption of Cr^{6+} ion is instantaneous and saturation of the different materials takes place after almost 1 h of contact between the adsorbent and the adsorbate, except in the case of RHA200 treated in air at 200 °C, whose adsorption-desorption equilibrium is reached at around 3 h of contact. It is probable that stabilization of the organic matter of RH at this temperature has not yet occurred.

The results of adsorption capacity of the different materials obtained by physical activation of RH are given in Table 9.3. It appears that the RHA250 material exhibits the best adsorption capacity compared to other materials (RHA350 and RHA450). The adsorption performance decreases as the treatment temperature increases. The adsorption efficiency of RHA250 material can be linked to the existence of surface functions created at that temperature (presence of a C=O band around 1720 cm^{-1} on the RHA250 IR spectrum hardly observed on the spectra of samples RHA350 and RHA450). In consequence, the temperature value of 250 °C is chosen as optimal temperature for the chemical activation of RH.

The chemical activation of RH was conducted under the following experimental conditions: A mass of RH was added to 20 mL of dilute phosphoric acid 80% in distilled water (% acid in the mixture). These ingredients were well mixed to a paste that was introduced into a basket, and then heat-treated in air in an electric furnace set horizontally. The material obtained, labelled RHP250, was washed with distilled water using a Soxhlet apparatus to remove the excess phosphoric acid, then dried and weighed to determine the yield of carbonization.

9.2.6 Adsorption Isotherms

In order to describe the performance of the obtained adsorbents using MB, two adsorption models we used; Langmuir and Freundlich models (Langmuir 1918; Freundlich 1906).

Table 9.4 Parameters of the Langmuir and Freundlich equations for adsorption of methylene blue onto different samples

	Langmuir			Freundlich		
Sample	Q_{max} (mg/g)	b	R^2	k_f (mg/g)	n	R^2
RHA250	212	0.076	0.99	25.32	0.516	0.97
RHP250	667	0.067	0.99	47.4	0.71	0.99
RHP450	333	0.030	0.99	14.94	0.69	0.99

The Langmuir equation is expressed in the case of the adsorption solution (Giles and Nakhwa 1962):

$$1/Q_e = 1/Q_{max} + 1/\left(kQ_{max}C_e\right)$$

where:

Q_e: the adsorption capacity at equilibrium (mg/g).
Q_{max}: the maximal adsorption capacity (mg/g).
C_e: the residual concentration (mg/L).
k: the thermodynamic adsorption constant (L/mg).

The Freundlich equation is well suited to describe the system in aqueous phase. The equation used in the linear form (Freundlich 1906) is:

$$\log Q_e = \log K_f + n \log C_e$$

Q_e: the adsorption capacity at equilibrium (mg/g).
C_e: the equilibrium concentration of solute in the aqueous phase (mg/L).
K_f and n: constants of Freundlich model linked to the adsorption capacity and the intensity, respectively.

The isotherm constants and obtained coefficients of the Langmuir and Freundlich equations were summarized in Table 9.4. The data from this table shows that the sample RHP250 has a maximum surface adsorption compared to other samples. The relatively low values in the case of the sample RHA250 confirm the important role phosphoric acid plays in protecting organic matter and the creation of porosity. The values of maximal adsorption capacity, of the MB, obtained from the Langmuir and Freundlich models are 667 and 47.4 mg/g, respectively. This value is higher than that of activated carbons reported in previous works (Ichcho et al. 2005; Castro et al. 2000b; Bacaoui et al. 1998).

9.3 New Porous Ceramics Based on Natural Clay and Moroccan Oil Shale

Our objective was to study the possibility to produce new porous ceramics by mixing clay and oil shale. This section is aimed at studying the use of Moroccan oil shale as a porogen for ceramic membrane manufacturing and investigating the effect of oil shale loading on the microstructure and mechanical properties of clay-based porous ceramic supports prepared by uniaxial compaction. Additionally, MF ceramic membranes were prepared by spin coating a suspension of micronized clay powder on the inner surface of the above supports and applied to the treatment of two different effluents.

Natural red clay from the Safi region (Morocco), used as a raw material for manufacturing porous ceramic supports and membrane layers, was crushed into small fragments and ground into a fine powder (<150 μm).

9.3.1 Fabrication of Porous Ceramic Supports

Mixtures of raw clay and oil shale (1:1 w/w) were prepared at room temperature by dry mixing. The mixtures were homogenized using a rotary mixer for 1 h. Then the powders were uniaxially pressed at 8 MPa in a stainless steel die (D: 22 mm) for 10 min. The compacted pellets were heated at 1000, 1050, and 1100 °C. Sintering was carried at selected temperatures using a heating rate of 10 °C min^{-1} and a 2 h dwelling at the maximal temperature. Three samples were prepared under the conditions described above: **sample 1** sintered at 1000 °C, **sample 2** sintered at 1050 °C, and **sample 3** sintered at 1100 °C (Fig. 9.5).

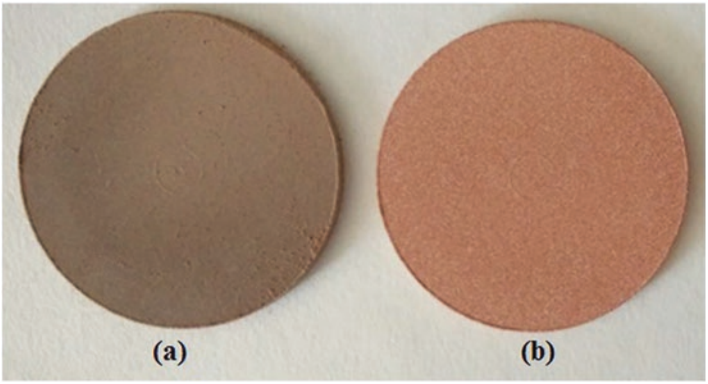


Fig. 9.5 Images of obtained ceramic membrane: Before (**a**) and after (**b**) sintering

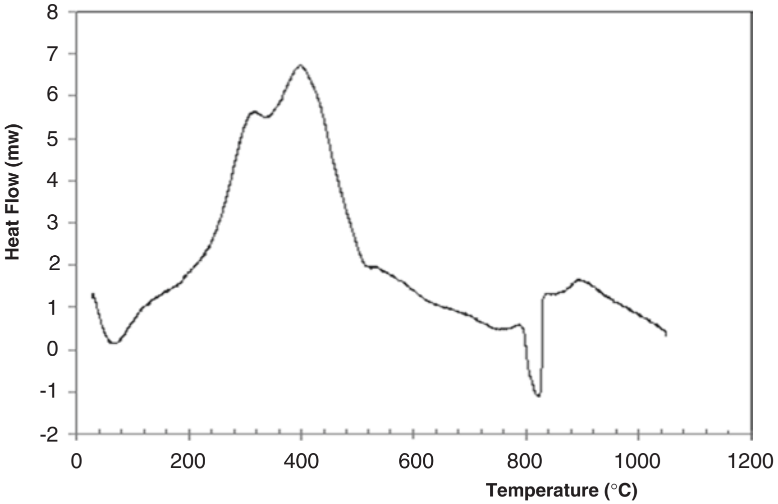


Fig. 9.6 DTA plot of a 50:50 wt% oil shale/clay mixture

9.3.2 Characterization of Porous Ceramic Support

9.3.2.1 DTA Analysis

First, in order to study the behavior of the mixture of raw clay and oil shale during heat treatment, an analysis was performed by DTA. The DTA plot (Fig. 9.6) presents four areas: the first, between 60 °C and 130 °C, is due to elimination of water. The second (from 320 °C to 470 °C) is caused by the decomposition of the organic matter of the oil shale. The third, in the range 500–670 °C, is due to dehydroxylation of clay minerals. The fourth, in the range 750–870 °C, corresponds to the decomposition of carbonates, essentially calcite and dolomite. In fact, it is admitted that dolomite $CaMg(CO_3)_2$ decomposes first between 700 and 800 °C to form MgO. In contrast, calcite $CaCO_3$ decomposes at a higher temperature (Campbell 1978). Next, to appreciate the potential of oil shale as an additive to produce porous ceramics, three samples were prepared under the conditions described in the experimental part: **sample 1** sintered at 1000 °C, **sample 2** sintered at 1050 °C, and **sample 3** sintered at 1100 °C.

9.3.2.2 Porosity and Density

The results of MIP analyses are shown in Table 9.5. We note that the porosity almost doubled compared with the samples obtained using clay only. These results show that the oil shale, highly rich in organic matter, can be used as natural and low-cost porogen agent for the development of porous ceramics. S**ample 3** sintered at 1100 °C having the highest porosity. The increase in porosity with oil shale addition may be due mainly to the increase of CO_2 gas released from the thermal decomposition of both organic matter and carbonates.

Table 9.5 Effect of sintering temperature on densification and flexural strength for materials prepared by mixing clay and oil shales

Samples	Temperature (°C)	Porosity (%)	Bulk density (g·cm^{-3})	Apparent density (g·cm^{-3})	Flexural strength (MPa)
Sample 1	1000	40.85	1.66	2.82	15.2 ± 0.9
Sample 2	1050	38.64	1.66	2.71	18.2 ± 2.7
Sample 3	1100	43.89	1.52	2.72	22.1 ± 2.1

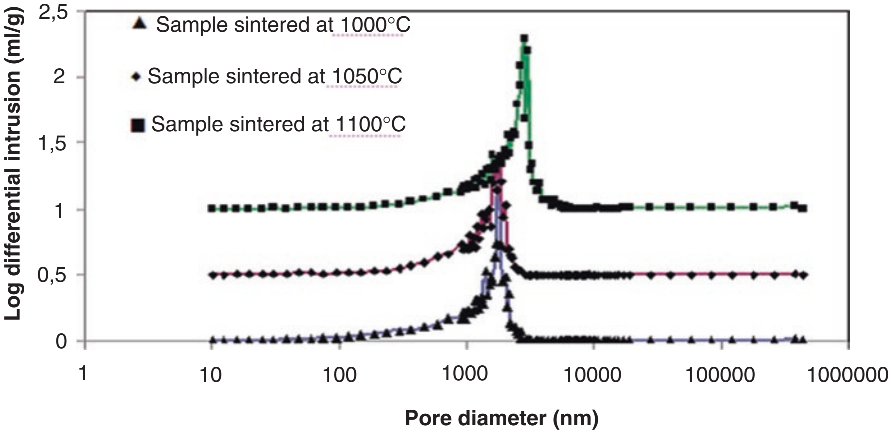


Fig. 9.7 Pore size distribution of samples prepared by mixing clay and oil shales

9.3.2.3 Pore Size Distribution

The pore size distributions of the samples are shown in Fig. 9.7. The porous structure is uniform, all materials having almost 90% of the pores with diameter within the range 1.5–3 μm, which corresponds to macroporous ceramics.

9.3.3 SEM Imaging

Figure 9.8 illustrates SEM micrographs of the macroporous ceramics sintered at three different temperatures. All the samples showed a surface with rough morphological structure. **Sample 3,** sintered at the highest temperature, shows highly porous structure compared to other samples, which corroborates the results of MIP analyses.

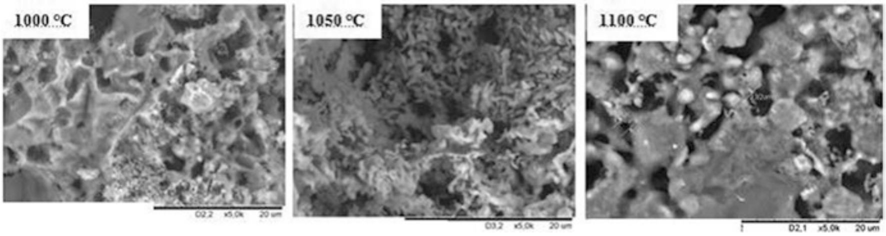


Fig. 9.8 SEM micrographs of samples prepared by mixing clay and oil shales

9.3.4 Mechanical Properties

The mechanical resistance test was performed using the three points bending strength to control the resistance of the samples fired at different temperatures. The mechanical strength reported in Table 9.5 increases with increasing sintering temperature and reaches 22.1 ± 2.1 MPa at 1100 °C. This value is relatively lower than that of porous ceramic prepared from clay reported in previous works (Saffaj et al. 2004; El Moudden et al. 2001). The gradual improvement in mechanical properties observed when the temperature increases from 1000 to 1100 °C is linked possibly to the formation of mullite, a phase known for its good mechanical properties (Rendtroff et al. 2009; Rendtroff et al. 2008; Soro 2003).

The material obtained at a firing temperature of 1100 °C (**sample 3**) was selected to study its elastic properties and behavior during the diametral compression test (Brazilian test). The shape of the load-displacement curve in **Fig.** 9.9 confirms the linear elastic and brittle behavior determined by the three-point bending test. The load was first gradually increased and then increased linearly up to rupture. This is probably attributable to the compression of pores during loading. The tensile strength value is 8.5 MPa. The decrease in tensile strength is attributed to the increase of pore size and open porosity, in perfect agreement with the theoretical model described by Dean et al. (Dean and Lopez 1983).

The evolution of dynamic elastic properties determined by ultrasonic non-destructive testing of **sample 3** are summarized in Table 9.6. The Young's modulus (E) and Poisson's ratio (ν) values obtained at 1100 °C are relatively higher than that reported in the literature for clay ceramics, namely by Lee and Yeh (Lee and Yeh 2008) and by Aston et al. (Aston et al. 2002).

9.3.5 Chemical Resistance to Acid/Alkali Corrosion

Figure 9.10 shows the weight loss of the produced porous ceramic based on oil shales soaked in an acid/alkali solution for different periods. The obtained ceramic exhibited a weight loss of up to 7.8% after soaking in HNO_3 solution (pH 1). The poor acid-corrosion resistance of the fabricated porous ceramic can be attributed to the quick dissolution of Mg and Al elements derived from clay (Dong et al. 2007).

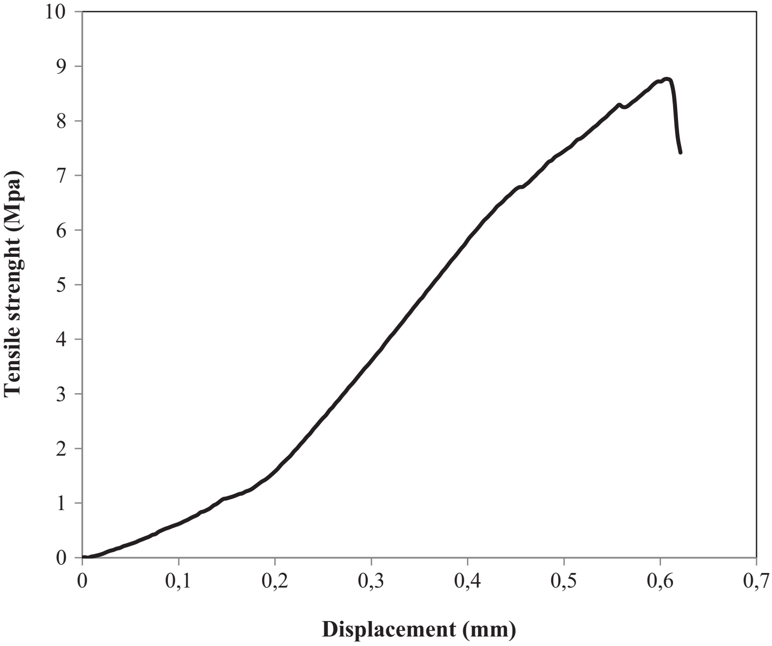


Fig. 9.9 Typical load–displacement curve of sample 6 sintered at 1100 °C under diametral compression

Table 9.6 Elastic properties of sample 6 sintered at 1100 °C

Property	Value
Apparent density (g·cm^{-3})	1.67
Longitudinal velocity (m·s^{-1})	3372
Transversal velocity (m·s^{-1})	2099
Young modulus E_D (GPa)	17.37
Shear modulus G (GPa)	7.34
Poisson ratio ν	0.18

In contrast, in the concentrated NaOH solution the mass loss is almost negligible, which shows their potential application in the pre-treatment of strongly basic media.

9.3.6 Filtration Test

For the filtration test, the optimal ceramic membrane sintered at 1100 °C was used for the treatment of two industrial effluents. Effluent A was collected from a Fes tannery beamhouse. In particular, the beamhouse process features the following phases: (1) soaking (rehydration and desalination of skin), (2) liming (dehumidification by sulfides), (3) washing (water and sodium bisulfide), (4) delimitation (using (organic) acids or mineral salts), (5) bating (enzymatic treatment), and (6)

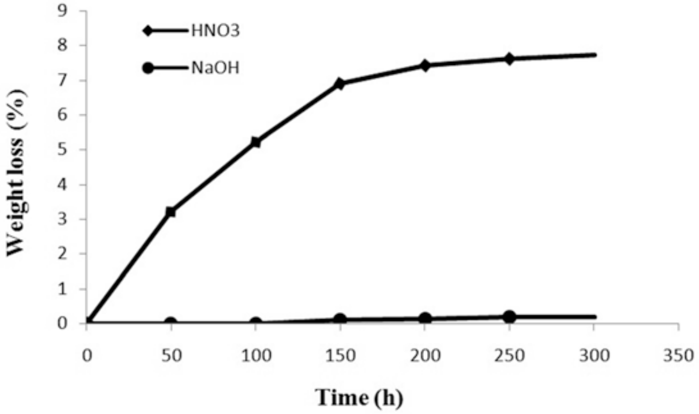


Fig. 9.10 Weight loss of the sintered porous ceramic in nitric acid (pH 1) and sodium hydroxide (pH 13) solutions as a function of time

acidification (tanning material penetration), which generate large amounts of turbid water that needs to be filtered and recycled (Khemakhem et al. 2017b). Effluent B is the wastewater discharged during the jeans washing process. Since most operations in the textile industry consume significant quantities of water and produce large amounts of poisonous substances and other chemical species, textile effluents are characterized by high concentrations of pollutants and a wide variety of compositions that reflect the variability of the employed technological processes. In particular, colored textile industry sewage typically contains high amounts of dyes, suspended solids, colloids, and dissolved organic carbon (Arslan et al. 2016). Fig. 9.11 presents the photographs of (a) tannery and (b) textile effluents before (1) and after (2) treatment using ceramic support. As shown in Fig. 9.11, one can note that the filtration of tannery and textile effluents through the ceramic support revealed highly effective contaminant removal and reduced turbidity, residual dye content, and suspended solids. This is in agreement with the results obtained in our previous works (Mouiya et al. 2019; Mouiya et al. 2018b).

9.4 Conclusions

Within the framework of the development of Moroccan natural resources, we have carried out a study on Tarfaya oil shale in order to prepare new porous materials from Moroccan natural resources. Based on the results of this study, the following conclusions can be made:

- Tarfaya oil shale can be a suitable adsorbent for the removal of metals or organics from water and wastewater, as both kinetics and capacity are highly favorable.

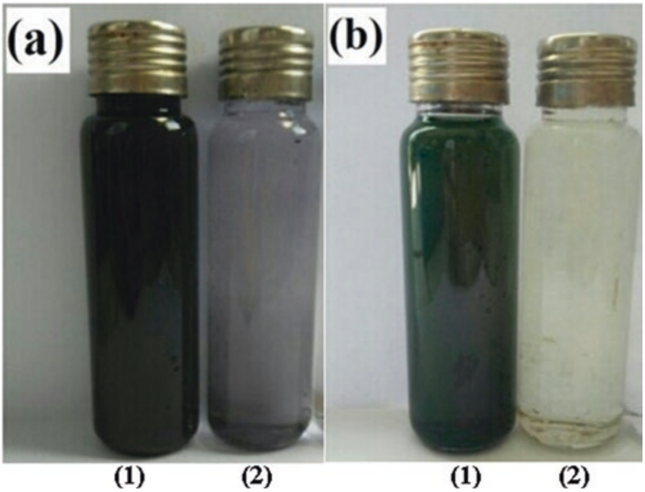


Fig. 9.11 Views of effluents before (1) and after (2) treatment using ceramic support: (**a**) tannery wastewater and (**b**) textile effluent

- Materials adsorbents produced in this work possess high adsorption capacity compared to others reported in the literature.
- The chemical activation with phosphoric at low temperature (250 °C) of the oil shale produces a material with a good yield (~70%), a high specific surface area (~600 m^2/g), and a highly porous structure, which gives it a high retention of methylene blue and Cr^{6+} ion.
- Porous ceramics with good mechanical properties and high porosity can be prepared from 1:1 mixtures of oil shale and clay.
- The filtration of tannery and textile effluents through the membrane revealed highly effective contaminant removal and reduced turbidity, residual dye content, and suspended solids.
- The produced ceramic membrane based on the clay and oil shale could be a perfect candidate for prepurification of strongly alkaline industrial waste liquids because of its low cost, easy fabrication, and high turbidity removal efficiency.

References

Abourriche A, Oumam M, Larzk M, Ichcho S, Hannache H, Pailler R, Naslain R, Birot M, Pillot J-P (2003) Elaboration et caractérisation des brais à partir des schistes bitumineux de Tarfaya (Maroc). Phys Chem News 11:10–15

Achiou B, Elomari H, Bouazizi A, Karim A, Ouammou M, Albizane A, Bennazha J, Alami Younssi S, El Amrani IE (2017) Manufacturing of tubular ceramic microfiltration membrane based on natural pozzolan for pretreatment of seawater desalination. Desalination 419:181–187

Arslan S, Eyvaz M, Gürbulak E, Yüksel E (2016) A review of state-of-the-art technologies in dye containing wastewater treatment – the textile industry case. In: Kumbasar EA (ed) Textile wastewater treatment. Intech, London, pp 1–28

Aston SD, Challis RE, Yiasemides GP (2002) The dependence of the elastic properties of silica/alumina materials on the conditions used for firing. J Eur Ceram Soc 22:1119–1127

Bacaoui A, Yaakoubi A, Dahbi A, Bennouna C, Ayele J, Mazet M (1998) Characterization and utilisation of a new activated carbon obtained from Moroccan olive wastes. J Water SRT-Aqua 47:68–75

Bekri O, Ziyad M (1991) Synthesis of oil shale research and development activ-ities in Morocco, in: Institute of Mining and Minerals Research (Ed.), Proceedings of eastern oil shale symposium, Lexington, Kentucky, USA, pp. 437–443

Benaddi H, Bandosz TJ, Jagiello J, Schwarz JA, Rouzaud JN, Legras D (2000) F. B'eguin, surface functionality and porosity of activated carbons obtained from chemical activation of wood. Carbon 38(5):669–674

Benadjemia M, Millière L, Reinert L, Benderdouche N, Duclaux L (2011) Preparation, characterization and Methylene Blue adsorption of phosphoric acid activated carbons from globe artichoke leaves. Fuel Process Technol 92:1203–1212

Bestani B, Benderdouche N, Benstaali B, Belhakem M, Addou A (2008) Methylene blue and iodine adsorption onto an activated desert plant. Biotech 99:8441–8444

Campbell JH (1978) The kinetics of decomposition of Colorado oil shale: II: carbonate minerals UCRL52089, Part 2, 13 mars 1978

Castro JB, Bonelli PR, Cerrella EG, Cukierman AL (2000a) Phosphoric acid activation of agricultural residues and bagasse from sugar cane: influence of the experimental conditions on adsorption characteristics of activated carbons. J. Ind. Eng. Chem. Res. 39:4166–4172

Castro JB, Bonelli PR, Cerrella EG, Cukierman AL (2000b) Phosphoric acid activation of agricultural residues and bagasse from sugar cane: influence of the experimental conditions on adsorption characteristics of activated carbons. J Ind Eng Chem Res 39:4166–4172

Cavalier JC, Chornet E (1978) Fractionation of peat-derived bitumen into oil and asphaltenes. Fuel 57:304–308

Dabir S, Deng W, Sahimi M, Tsotsis T (2017) Fabrication of silicon carbide membranes on highly permeable supports. J Membr Sci 537:239–247

Dean EA, Lopez JA (1983) Empirical dependence of elastic moduli on porosity for ceramic materials. Journal of Am Cer Soc 66:366–370

Dong Y, Feng X, Dong D, Wang S, Yang J, Gao J, Meng G (2007) Elaboration and chemical corrosion resistance of tubular macro-porous cordierite ceramic membrane supports. J Membr Sci 304:65–75

El Moudden N, Elghazouali A, Rakib S, Sghyar M, Rafiq M, Larbot A, Cot L (2001) Nouveaux supports membranaires à base de chamotte d'argile. Ann Chim 26:5–1

Fan P, Zhen K, Zan Z, Chao Z, Jian Z, Yun J (2016) Preparation and development of porous ceramic membrane supports fabricated by extrusion technique. Chem Eng Trans 55:277–282

Freundlich HMF (1906) Uber die adsorption in losungen. J Phys Chem 57:385–470

Giles CH, Nakhwa SN (1962) J App Chem 12:266

Ichcho S, Khouya E, Fakhi S, Ezzine M, Hannache H, Pallier R, Naslain R (2005) Influence of the experimental conditions on porosity and structure of adsorbents elaborated from Moroccan oil shale of Timahdit by chemical activation. J Hazard Mater A118:45–51

Jaguaribe EF, Medeiros LL, Barreto MCS, Araujo LP (2005) The performance of activated carbons from sugarcane bagasse, babassu and coconut shells in removing residual chlorine. Braz J Chem Eng 22(1):41–47

Jeong Y, Lee S, Hong S, Park C (2017) Preparation, characterization and application of low-cost pyrophyllite-alumina composite ceramic membranes for treating low-strength domestic wastewater. J Membr Sci 536:108–115

Khemakhem I, Gargouri OD, Dhouib A, Ayadi MA, Bouaziz M (2017a) Oleuropein rich extract from olive leaves by combining microfiltration, ultrafiltration and nanofiltration. Sep Purif Technol 172:310–317

Khemakhem I, Gargouri OD, Dhouib A, Ayadi MA, Bouaziz M (2017b) Oleuropein rich extract from olive leaves by combining microfiltration, ultrafiltration and nanofiltration. Separ Purif Technol 172:310–317

Langmuir I (1918) Adsorption of gases on plain surfaces of glass mica platinum. J Am Chem Soc 40:136–403

Le NL, Nunes SP (2016) Materials and membrane technologies for water and energy sustainability. Sustainable Mater Technol 7:1–28

Lee VG, Yeh TH (2008) Sintering effects on the development of mechanical properties of fired clay ceramics. Mater Sci Eng A 485:5–13

Legrouri K, Khouya E, Ezzine M, Hannache H, Denoyel R, Pallier R, Naslain R (2005) Production of activated carbon from a new precursor molasses by activation with sulphuric- acid. J Hazard Mater 118:259–263

Molina-Sabio M, Rodriguez-Reinoso F, Caturala F, Sell'es MJ (1995) Porosity in granular carbons activated with phosphoric acid. Carbon 33(8):1105–1113

Moreno-Castilla C, Carrasco-Marin F, Lopez-Ramon MV, Alvarez-Merino MA (2001) Chemical and physical activation of olive-mill waste water to produce activated carbons. Carbon 39(7):1415–1420

Mouiya M, Abourriche A, Benhammou A, El Hafiane Y, Abouliatim Y, Nibou L, Oumam M, Hannache H, Smith A (2017) Porous ceramic from Moroccan natural phosphate and raw clay for microfiltration applications. Desalin Water Treat 83:277–280

Mouiya M, Abourriche A, Bouazizi A, Benhammou A, El Hafiane Y, Abouliatim Y, Nibou L, Oumam M, Ouammou M, Smith A, Hannache H (2018a) Flat ceramic microfiltration membrane based on natural clay and Moroccan phosphate for desalination and industrial wastewater treatment. Desalination 427:42–50

Mouiya M, Abourriche A, Bouazizi A, Benhammou A, El Hafiane Y, Abouliatim Y, Nibou L, Oumam M, Ouammou M, Smith A, Hannache H (2018b) Flat ceramic microfiltration membrane based on naturalclay and Moroccan phosphate for desalination and industrialwastewater-treatment. Desalination 427:42–50

Mouiya M, Abourriche A, Bouazizi A, Benhammou A, El Hafiane Y, Abouliatim Y, Ouammou M, Smith A, Hannache H (2019) Fabrication and characterization of a ceramic membrane from clay andbanana peel powder: application to industrial wastewater treatment. Mater Chem Phys 227:291–301

Ohji T, Fukushima M (2012) Macro-porous ceramics: processing and properties. Int Mater Rev 57:115–131

Rendtroff NM, Garrido LB, Aglietti EF (2008) Effect of the addition of mullite-zirconia to the thermal shock behavior of zircon materials. Mater Sci Eng A 498:208–215

Rendtroff NM, Garrido LB, Aglietti EF (2009) Mechanical and fracture properties of zircon-mullite composites obtained by direct sintering. Ceram Int 35:2907–2913

Saffaj N, Loukili H, Alami Younssi S, Albizane A, Bouhria M, Persin M, Larbot A (2004) Filtration of solution containing heavy metals and dyes by means of ultrafiltration membranes deposited on support made of Moroccan clay. Desalination 168:301–306

Samain L, Jaworski A, Edén M, Ladd DM, Seo D-K, Garcia-Garcia FJ, Häussermann U (2014) Structural analysis of highly porous γ-Al_2O_3. J Solid State Chem 217:1–8

Soro NS (2003) Ph.D. Thesis, Limoges University, France

Stawiskia B (2014) Research regarding effectiveness of compaction by compressing dry mortar cement and ceramic. Procedia Eng 91:412–417

Valix M, Cheung WH, McKay G (2004) Preparation of activated carbon using low temperature carbonisation and physical activation of high ash raw bagasse for acid dye adsorption. Chemosphere 56:493–501

Wang HE, Xi LJ, Ma RG, Lu ZG, Chung CY, Bello I, Zapien JA (2012) Microwave-assisted hydrothermal synthesis of porous SnO_2 nanotubes and their lithium ion storage properties. J Solid State Chem 190:104–110

Yürüm Y, Kramer R, Levy M (1985) Interaction of kerogen and mineral matrixof an oil shale in an oxidative atmosphere. Thermochim Acta 94:285–293

10 Organic Contaminants in Industrial Wastewater: Prospects of Waste Management by Integrated Approaches

Taghreed Al-Khalid, Riham Surkatti, and Muftah H. El-Naas

Abstract

The growing world population and industrial development have led to the generation of different new types of hazardous chemicals that can have detrimental impacts on the environment. Contamination of soil, air, and water is one of the major problems facing the industrialized world today. A major class of these chemicals is organic aromatic compounds such as phenolic substances, most of which are hazardous pollutants and highly toxic even at low concentrations. Industrial plants such as petroleum refineries and gas processing facilities are the main sources of phenolic compounds in wastewaters. Given the increased awareness in realizing sustainable development, the management of wastewater containing high concentrations of phenols represents major economic and environmental challenges to the oil and gas industry. With emphasis placed on green technology, biotechnology has proved to play a vital role in the development of an economical approach for the effective removal of many organic water pollutants. Most of the recent research in the area has been focusing on developing new types of reactor systems and effective biocatalysts for the biodegradation of major contaminants in industrial wastewater. This chapter highlights the different options for the treatment of industrial wastewater with more focus on integrated systems of combined biological and physiochemical processes for the treatment of industrial effluents in an ecologically favorable process.

Keywords

Wastewater · Biotreatment · Integrated processes · Organic contaminants

---

T. Al-Khalid
Chemical and Petroleum Engineering Department, UAE University, Al-Ain, UAE

R. Surkatti · M. H. El-Naas (✉)
Gas Processing Center, College of Engineering, Qatar University, Doha, Qatar
e-mail: muftah@qu.edu.qa

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_10

10.1 Introduction

The expansion of several industries such as olive mills, chemical plants, pulp and paper, oil refineries, coal plants, and petrochemical industries resulted in the production of a significant quantity of wastewater (Pérez et al. 2016; Li et al. 2005; Santos et al. 2015). The industrial wastewater (IWW) characterization depends on the process type and configuration and is characterized with its high concentrations of organic and inorganic pollutants and some micro-pollutants and suspended particles that are typically presented in several wastewater streams (Santos et al. 2015). Moreover, the health and environmental impact of IWW is based on several characteristics, such as total phenols, total organic compounds (TOC), chemical oxygen demands (COD), biological oxygen demands (BOD), organic and inorganic contents, and amount of dissolved and suspended solids (Sonune and Ghate 2004). Generally, some industries such as olive mill, textile, and refining processes generated high strength wastewater characterized by dark color, foul-smell, high COD content, and phenols concentration (Dermeche et al. 2013). These organic pollutants are toxic and can cause an adverse effect on human health and aquatic life. Thus, it is essential to apply adequate treatment techniques before discharging into water bodies.

Chemical pollution caused by the presence of organic compounds is one of the main threats to water standards and quality. Several physical and chemical techniques such as Fenton's oxidation, electrocoagulation, filtration, adsorption using activated carbon, and ozonation were applied to reduce the concentration of toxic compounds to the acceptable limit (El-Naas et al. 2010a; Ahn et al. 1999). Compared to these techniques, biological treatment is generally applied in the area of wastewater treatment due to several advantages. Bio-treatment is inexpensive, environment-friendly, and results in complete mineralization of toxic pollutants; it can also be integrated and combined with other treatment techniques to obtain an efficient and cost-effective wastewater treatment. The treatment of high strength wastewater contaminated with high COD, BOD, and phenol contents using a single treatment process is a great challenge. There is no chemical or biological treatment technique that is known to be totally efficient, especially in terms of organic pollutant removal. Therefore, efforts have been made to develop more effective treatment processes, since no chemical, physical, or biological treatment approaches were found to be completely effective as a stand-alone technique, especially in terms of phenols, COD, and color reduction (Surkatti and El-Naas 2014).

In line with the quest for sustainable development and to comply with discharge legislation, the removal of organic contaminants from IWW is a major technological challenge. Water-management technologies and pollution-control strategies can be organized into hierarchal environmental preferences as (i) minimization, (ii) recycle/re-use, and (iii) disposal (when water management by the previous two options is not possible) (Jiménez et al. 2018). By environmental bylaws, further treatments need to be utilized to meet strict allowable limitations. Since the characteristics of IWW widely differ from one influent to another, the characterization of the IWW to determine main constituents is the first step in the selection of the optimum treatment for IWW, with consideration of environmental and economic aspects as well as the local regulatory framework. Furthermore, an inclusive knowledge of the different treatment options is essential in order to comply with effluent discharge standards. Prabakar et al. (2018) provided a comprehensive review on the various aspects of treatment in five major industries, namely, the paper and pulp mills, coal manufacturing facilities, petrochemical, textile, and the pharmaceutical industries. The treatment methods were classified into traditional methods usually carried out in a single step, and hybrid or combined (integrated) methods.

In general, IWW treatment goes through three main stages: pre-treatment, main treatment step, and final polishing treatment step. Different treatment methods used for degrading industrial organic waste can be classified under the following three categories: physical, chemical, and biological. In the category of physical methods, adsorption and membrane filtration are the most commonly used processes. The most common chemical process used for the treatment of effluents is oxidation. Recently, advanced oxidative processes (AOPs) such as photocatalytic degradation, microwave-assisted catalytic wet air oxidation, and Fenton process have gained considerable attention due to their ability to degrade a wide variety of organic substances by chemical oxidation, leading to complete mineralization. Diya'uddeen et al. (2011) and Rasalingam et al. (2014) reviewed the different treatment technologies for IWW, focusing on photocatalytic degradation as an AOP. Besides these conventional physical and chemical methods, various biological methods are used for the degradation of these organic pollutants. Biological methods employ the metabolic and enzymatic capabilities of microbes for the detoxification or mineralization of pollutants. The microorganisms use the carbon contained in the organic waste for their metabolism and convert the toxic contaminants into less harmful intermediates and byproducts.

A combination of physical, chemical, and biological treatment processes is strongly recommended. In a comparative study, Singh and Borthakur (2018) addressed biodegradation and photocatalytic degradation as two widely used techniques for the degradation of organic pollutants and urged the integration of biological and photocatalysis processes for efficient degradation of organic waste in IWW.

In the following subsections, physical, chemical, biological, and combined integrated techniques for the treatment of IWW are discussed in more detail.

10.2 Current Treatment Options

10.2.1 Physical Treatment

10.2.1.1 Flotation

Flotation is a widely used, cost-effective separation technique for wastewater treatment and for several mineral and biological industries. In this technique, air, nitrogen, or any inert gas is injected to capture components like suspended particles, oil droplets, and contaminants from the mixture stream based on their hydrophobic or hydrophilic surface properties (Al-Ghouti et al. 2019).

Flotation techniques consist of four basic steps: (i) air bubble generation; (ii) contact between the gas bubbles and oil droplets; (iii) attachment of the gas bubbles to oil droplets; and (iv) ascent of air-oil combination, provided that this aggregate has a much lower density than water itself.

In a review by Prakash et al. (2018), the details of various design parameters of the flotation process and the effect of operating and geometric variables affecting the separation efficiency are described. A novel process that used low-density glass microspheres instead of air and gas bubbles has also been reported (Jiménez et al. 2018).

10.2.1.2 Adsorption

Dissolved organics can easily be adsorbed on activated carbon, co-polymers, zeolites, and other resins (Singh and Borthakur 2018). Adsorption is one of the most commonly used wastewater treatment processes because of its simple design and convenient operation as well as its low cost compared with other treatment processes. It is often used at the end of a treatment sequence owing to the high purification efficiency (Al-Ghouti et al. 2019; Bel Hadjltaief et al. 2018).

Organic compounds and some heavy metals present in industrial waste get adsorbed on the porous surfaces of the activated carbon. For a long time, activated carbon has been the most widely used adsorbent to remove non-degradable hydrocarbon pollutants from contaminated wastewater (Singh and Borthakur 2018). It is featured as an effective adsorbent due to its large surface area and high adsorption capacity. However, one of the o main drawbacks of adsorption is the transfer of the pollutants from the IWW onto a solid matrix (Rasalingam et al. 2014), leading to the formation of serious by-products. This often necessitates regeneration of the activated carbon for reuse and disposal of the produced waste and spent media; the high cost of commercial activated carbon and difficult recovery from treated effluents limit its use as an adsorbent (Bel Hadjltaief et al. 2018). El-Naas et al. (2010a) presented a general discussion on activated carbon adsorption, its mechanism, and adsorption isotherms.

To tackle the drawbacks of the adsorption process and make it more competitive, other alternative adsorbents have been proposed. Biochar is defined as “a carbon-rich solid material from the thermo-chemical conversion of biomass (e.g. wood, manure, and leaves, etc.) at temperatures below 900 °C, in an oxygen-limited environment” (Zhang et al. 2019). There is a growing interest in the utilization of biochar as a promising adsorbent for the removal of various contaminants in IWW, thanks to its high specific surface area and high affinity toward heavy metals and organic contaminants. Biochar is inexpensive and can be easily prepared from a variety of readily available resources (Zhang et al. 2019).

The efficacy of activated carbons derived from electronic waste of CDs and DVDs, as low-cost carbonaceous materials, coated with carbon nanotubes was evaluated for the adsorption of a textile dye in aqueous solutions (Noorimotlagh et al. 2019). Ahmad et al. (2019) considered the incorporation of metals into ordered mesoporous carbon (OMC) for enhanced adsorption of dyes. A 40% increase in the overall adsorption capacity was observed compared to the non-modified OMC. In the context of green chemistry, natural clay was shown to be an innovative low-cost alternative to be used as an adsorbent for the removal of 2 chlorophenol. Characterized by its high iron content, it could also serve a dual purpose as a catalyst in the Fenton process (Bel Hadjltaief et al. 2018). Other novel synthetic clays (e.g., swelling micas) were evaluated for the removal of several priority pollutants (Martín et al. 2018). Sun et al. (2018) reported the easy fabrication of composition tunable 3D hierarchical bismuth oxyiodides, which have high adsorption capabilities and enhanced photocatalytic properties.

Considerable attention has been directed to the development of engineered nanoparticles (NPs) as an effective treatment technology of contaminated wastewater. In this regard, different types of engineered NPs have been developed as adsorbents. However, since the conventional production of NPs is linked with secondary environmental impacts and risks to human health, green synthesis is a key in the improvement of NP manufacturing in an effective and eco-friendly manner. Green synthesis procedures and resources have been successfully employed in the fabrication of many green NPs. This topic was extensively discussed in a critical review by Wang et al. (2019). An example of green synthesis of novel adsorbent NPs from an extract of waste tea was scrutinized for the removal of phenol red in a study by Gautam et al. (2018). A novel green synthetic procedure was also presented in a study by Ghobashy et al. (2018) for the potential fabrication of highly stable new selective polymeric materials for selective adsorption of chlorophenols from wastewater. A green process was also developed based on novel polymeric adsorption resins for the treatment of phenolic compounds in real effluent from the olive-oil industry (Ochando-Pulido et al. 2018).

10.2.1.3 Membrane Filtration

Membrane separation is an advanced technique that can be used for the removal of trace contaminants in IWW. Compared to conventional biological and physicochemical treatment methods, current membrane processes have the disadvantages of higher energy consumption and are more expensive. However, they are very promising in terms of continued improved performance by developing advanced membranes and filtration techniques. Membrane separation systems have many attractive characteristics including energy-efficient separation without phase change, small footprint, low generated quantities of sludge, as well as easy operation and maintenance (Alias et al. 2019). Diya'uddeen et al. (2011) reported that it has been a common practice not to use membrane separation for large volumes of effluent. Fouling is the main drawback of this technology, which results in higher operating pressure requirement and chemical cleanings for its prevention. Fouling often results in lowering the membrane's productivity, selectivity, flux, and its lifetime. Moreover, membrane separation usually results in transferring the organic pollutants to the rejection stream (Jiménez et al. 2018).

Reverse osmosis (RO) has become a widespread method for removing several toxic organic contaminants from IWW owing to its relative ease of use and reduced costs (Al-Obaidi et al. 2018a). Recently, RO technology has shown a lot of progress that is not limited to membrane materials, process design, and optimization but includes the adoption of the suitable pretreatment option that can alleviate organic and inorganic fouling by selectively excluding undesired compounds. This pretreatment targets the main challenge, that is, membrane fouling, and directly impacts RO system performance. Anis et al. (2019) provided a comprehensive critical review that addressed the major issues of conventional RO pretreatment methods and discussed the developments in classical and novel RO pretreatment methods, with special focus on microfiltration, ultrafiltration, and nanofiltration methods and their development in terms of advanced ceramic-based membranes and self-cleaning membranes.

The RO process has been considered by several authors for the removal of phenol and its derivatives from wastewater. Al Obaidi et al. (2018b) conducted a simulation and optimization study to explore the feasibility of an alternative RO process scheme that replaces a single stage design with two-stage/two-pass process configuration for improving the removal efficiency of chlorophenol. The energy-saving RO process was proposed as an alternative for the UV/H2O2 that consumes a lot of energy. A maximum efficiency of 93.3% chlorophenol removal has been obtained for the proposed configuration, with a reported 12.4% higher than the single-stage configuration.

Other than RO, microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) can also be used and different kinds of membranes have been tested. Polymeric membranes are susceptible to degradation due to thermal instability at temperatures exceeding 50 °C, and more sensitive to cleaning products (Jiménez et al. 2018). According to Alias et al. (2019), membrane separation for oilfield produced water treatment needs further improvement on robustness because of the complex viscous composition and high temperature of this type of water. Recently, ceramic membranes have attracted remarkable interest for the treatment of different industrial wastewaters owing to their outstanding characteristics over polymeric membranes such as superior durability, excellent mechanical and thermal stability, robustness, anti-bacterial resistance, and ease of cleaning. However, they still have the main disadvantage of high capital cost, coupled with the high energy demand for the recycle rates needed for fouling control, which results in increased operational costs (Jiménez et al. 2018). Therefore, there is a need to address challenges such as optimization of capital and fabrication costs by developing new technologies, improving selectivity and permeability, fouling minimization, and carrying out research on large-scale applications. Samaei et al. (2018) reviewed the studies performed on the utilization of pressure-driven ceramic membranes for the treatment of IWW. It was reported that the high capital cost of this technique is an obstacle that prevents its extensive use by the industry shareholders, in favor of polymeric systems for the treatment of industrial effluents. Thus, it is strongly recommended to carry out more research that is focused on increasing the economic competitiveness of ceramic membranes over polymeric membranes. Additionally, predictive and simulation models are needed to evaluate the profitability in large-scale applications.

10.2.2 Chemical Treatment

10.2.2.1 Chemical Precipitation

Precipitation is one of the most commonly used conventional chemical treatment processes of IWW, with reported removal efficiencies of suspended and colloidal particles up to 97%. Inorganic metals, such as iron, magnesium, and aluminum polymers, are normally used as flocculants and coagulants in the chemical precipitation process and proved to be effective in removing most organic pollutants (Al-Ghouti et al. 2019). Examples of other coagulants include inorganic mixed metal (Fe, Mg, and Al) polynuclear polymers, which are mainly beneficial for wastewaters with high levels of suspended solids, owing to their efficiency of deoiling as well as coagulation and anti-scale properties. However, coagulation and flocculation are suitable for the removal of suspended and colloidal matter but seem to be inefficient for removing dissolved substances (Jiménez et al. 2018).

10.2.2.2 Electrochemical Processes

They include two groups of processes: electrocoagulation, electroflocculation, electrodeposition, and electroflotation in one group and electrochemical oxidation in another group. This section is devoted to discussion on the first group comprising the more traditional electrochemical processes; whereas the second group will be considered in the section of chemical oxidation treatment. Compared to conventional treatments methods, electrochemical techniques are relatively inexpensive and do not generate secondary wastes nor require the use of additional chemicals. Furthermore, they can remove organic materials efficiently, with the frequently emphasized added benefit of valuable materials recovery from the treated wastewater, which is not the case with other treatment processes (Jiménez et al. 2018). To achieve a better quality of the end effluent, a good recommended choice is the integration of an electrochemical process unit with some other chemical processes, for example, AOP, to obtain cleaner end-use water (Jiménez et al. 2018). Various electrochemical techniques such as electrodeposition, fuel cell, photo-electrochemistry, photo-catalysis, and photo-electrocatalysis may be consolidated into one electrochemical process. Al-Khalid and El-Naas (Al-Khalid and El-Naas 2012) presented a more detailed discussion on electrocoagulation. They stated that the attraction of electrocoagulation is rather restricted by its rare and limited application in the literature for real wastewater treatment. Only a limited number of studies have addressed the real application and related performance and design of electrocoagulation (Rajkumar and Palanivelu 2004; Abdelwahab et al. 2009; El-Naas et al. 2009; Yavuz et al. 2010; Yan et al. 2014).

Fuel cells represent another highly promising electrochemical technology with a prospective potential for the IWW treatment. However, its successful application in the near future is still subject to reducing its cost, enhancing its efficiency, and extending its life span (Al-Ghouti et al. 2019). Photo-electrolysis is another chemical process that uses light for decomposing large molecules into smaller ones. It has been reported that the removal of organics from contaminated wastewater could be achieved using semiconductor photocatalysis, with high efficiency reaching 90% in a short time of 10 minutes (Al-Ghouti et al. 2019).

10.2.2.3 Chemical Oxidation

According to Singh (Singh and Borthakur 2018), oxidation is the most common chemical method used for the treatment of IWW effluents. The general concept is the breakdown of multiple contaminants using several oxidants such as oxygen, ozone, chlorine, and peroxide. The various crucial parameters that affect the oxidation rate are chemical oxidant type and dose, quality of the influent water, and its contact time with the used oxidant. Several benefits are attributed to this treatment option like the least requirement of equipment, no need for any pretreatment process, and the possibility of achieving almost 100% water recovery rate (Al-Ghouti et al. 2019). However, there are some issues linked to this treatment method such as the need to use a large quantity of chemicals and the high cost of these chemicals, low reaction rate, and the generation of sludge, which necessitates extra disposal treatment, in addition to the requirement of regular calibration of the chemical pump (Singh and Borthakur 2018; Al-Ghouti et al. 2019).

AOP has emerged as a recent development in water treatment that can offer effective solutions for oxidizing the several types of organic pollutants via the addition of oxidants or mixture of oxidants. These processes include a wide variety of techniques that utilize ozone, iron, and hydrogen peroxide as chemical oxidizers. Besides, hydroxyl radicals like zinc oxide, titanium dioxide, and iron oxide are also considered by this treatment method (Al-Ghouti et al. 2019). Due to the significance of AOPs as promising technologies for IWW treatment, it was thought necessary to discuss them in a separate subsection.

10.2.2.4 Advanced Oxidation Processes (AOP)

Since most of IWW treatment methods do not degrade the pollutant completely, but merely transfer it from the aqueous phase to another phase, AOP has received considerable attention as an efficient method for destroying multiple recalcitrant organic contaminants by chemical oxidation, leading to complete mineralization of the pollutant (Rasalingam et al. 2014; Singh and Borthakur 2018). Another merit is that the required treatment can take a very short time depending on the wastewater characteristics (Jiménez et al. 2018). However, the drawbacks include high maintenance cost and the need for skilled manpower (Singh and Borthakur 2018). Generation of powerful oxidizing agents, mainly hydroxyl, is a common objective shared by all AOPs. Hydroxyl radical breaks down complex organic compounds into carbon dioxide, water, and inorganic ions (Jiménez et al. 2018; Prabakar et al. 2018). There are two pathways for the production of hydroxyl radicals: anodic oxidation (direct form) and mediated electrooxidation (indirect form). These technologies comprise a diversity of processes such as indirect electrochemical oxidation using ozone, hydrogen peroxide, and ferrate; Fenton reaction and photo-

Fenton reaction; in addition to non-conventional AOPs, such as wet air oxidation, supercritical water oxidation (Jiménez et al. 2018), and microwave-assisted oxidation (Shiying et al. 2009).

Fenton processes are considered very efficient methods for producing active hydroxyl radicals through hydrogen peroxide (H2O2) decomposition catalyzed by ferrous iron (Fe2+). Other modified methods were developed to carry out non-classical Fenton reaction with the goal of achieving higher decontamination efficiency, less harmful byproducts, and saving on energy and chemical consumption. Radwan et al. (2019) utilized the electro-Fenton process for the removal of benzene (B), toluene (T), and p-xylene (X) (BTX) from aqueous solutions using different electrodes. Complete degradation of BTX was achieved within 30 minutes under recommended preferable conditions.

Garcia-Segura et al. (2018) reviewed the application and performance of electrochemical advanced oxidation process over the treatment of real industrial and urban effluents, with focus on the treatment of industrial effluents resulting from textile dyeing, petrochemical, paper mill, and tannery industry. In addition, potential combination and integration schemes of electrochemical oxidation and other wastewater treatment technologies are also examined.

10.2.3 Biological Processes

Biological treatment is considered as one of the least expensive and most attractive methods for removal of different kinds of contaminants from IWW, with either aerobic or anaerobic prevailing conditions (Jiménez et al. 2018; Singh and Borthakur 2018; Al-Ghouti et al. 2019)). Catalysis by the enzymatic activity of microorganisms such as bacteria, algae, and fungi plays a key role in biological oxidation, where dissolved organics and ammonia are mineralized into water and CO_2 and nitrates/nitrites, respectively. Two leading mechanisms in this transformation are biodegradation and bioflocculation. In biodegradation, microorganisms break down hydrocarbon substances into smaller molecules and use them for their metabolism as carbon and energy sources. Bioflocculation is induced by the presence of suspended sludge, where flocs (activated sludge) adsorb soluble and insoluble materials within their own matrix. The physical mechanical separation of those flocs results in the removal of these materials. On the other hand, anaerobic treatment could also serve as a cost-effective alternative to biological oxidation in cases of IWW with a high organic load (Jiménez et al. 2018).

Multiple different processes and techniques like sequencing batch reactors, trickling filters, rotating biological contactor (RBC), and biological aerated filters can be considered for biological treatment of IWW (Singh and Borthakur 2018; Al-Ghouti et al. 2019). A conventional activated sludge process has long been employed as the standard and widespread biological treatment of IWW, within an integrated system that incorporates mechanical and physiochemical pre-treatment

(El-Naas et al. 2014a). It has been reported that activated sludge treatment can achieve 98–99% removal efficiency of petroleum hydrocarbons within a retention time of about 20 days (Jiménez et al. 2018; Al-Ghouti et al. 2019). Conventional activated sludge systems are designed with two physically separate tanks such as (i) an aeration tank in which biological mineralization reactions take place and (ii) a settling tank in which activated sludge is separated from the decontaminated water by flocculation. This separation of aeration and settling tanks is a drawback of the process, in addition to low biomass concentrations in the aeration tank, the requirement of large floor area, and high energy demand for aeration and recycling utilities (Nancharaiah and Kiran Kumar Reddy 2018).

Although biodegradation is a suitable and attractive technology for decontamination of IWW, conventional processes suffer from the inhibition effect at high concentrations of toxic substances (Liao et al. 2018). Immobilized cell reactors significantly improve bacterial activity and show superior characteristics over suspended cell reactors (Al-Khalid and El-Naas 2018). Basak et al. (2019) evaluated the efficiency and reusability of sugarcane bagasse as a low-cost immobilization support matrix for Candida tropicalis PHB5 in recirculating up-flow packed bed reactor (PBR) for effective biodegradation of high strength phenol. In another study (Ruan et al. 2018), batch biodegradation of phenol was investigated under different conditions, using Sphingomonas sp. GY2B, immobilized in polyvinyl alcohol (PVA)–sodium alginate–kaolin beads.

Biofilm processes are categorized as attached (immobilized) growth and suspended growth processes. Biofilm systems can also be grouped into fixed-medium systems and moving-medium systems. In fixed-medium systems, the biofilm media are stationary in the reactors; examples include trickling filters and biological aerated filters. Alternatively, RBCs, moving-bed bioreactors (MBBRs), fluidized bed bioreactors (FBBRs), and spouted bed bioreactors (SBBRs) are examples of moving-medium systems. Abu Bakar et al. (2018) reviewed the advantages and challenges of using MBBR technology as applied to effluents of palm oil mill with the target of achieving the goal of “zero effluent discharge.” Moreover, the integration of moving-bed biofilm reactors and other treatment processes, such as membranes and coagulation, is also discussed. It was pointed out that, compared to conventional systems, MBBR can attain high COD reduction rates while occupying less space.

In recent years, much attention has been focused on aerobic granules developed in sequencing batch reactors (SBRs) (Al-Khalid and El-Naas 2018). Marked as a novel technology, it can overcome some of the restrictions of conventional activated sludge systems, whereas its concept relies on the growth of dense granulated biomass via self-immobilization. Additionally, it is a more sustainable wastewater treatment option. Detailed information on aerobic granulation can be found in a review by Khan et al. (2013). Nancharaiah and Kiran Kumar Reddy (2018) reviewed the status of research on aerobic granulation technology and its applications. It was concluded that this technology has evidence for prominent settling features and biodegradation capability of toxic or recalcitrant pollutants. Because of its unique characteristics, the aerobic granulation technology has been considered particularly effective for the treatment of high strength wastewater containing various contaminants, such as organics, nitrogen, and phosphorus. Aerobic granules were successfully used in SBR for the simultaneous pyridine biodegradation and nitrogen removal (Liu et al. 2018a).

Simultaneous treatment of wastewaters with the recovery of clean energy can be achieved by the microbial fuel cell (MFC). In this regard, different configurations, MFC designs systems, and electrode assemblies have been devised for the treatment of IWW using native or enhanced electrogenic microorganisms. Hui Liu et al. (2018b) used polyvinyl alcohol hydrogel in an innovative modification of the cathode in an MFC to promote the generation of electricity and for the enhancement of toluene removal from contaminated water. Another study (Hassan et al. 2018) demonstrated successful biodegradation of 2, 4 dichlorophenol in parallel with electricity production. Microbial desalination cell (MDC) is a newly developed multi-purpose technology that originated from the traditional MFC process to serve for electricity generation, water desalination, and wastewater treatment. A reactor design which incorporates a desalination chamber in-between the cathode and the anode chambers was employed for this purpose (Al-Ghouti et al. 2019).

The treatment of different types of IWW effluents has been extended to include the use of constructed wetlands. A pilot scale study by Mustafa et al. aimed at examining the performance of free water surface wetland for its potential to treat different hydrocarbons present in produced water from a gas field. Under local environmental conditions, the study proved the steady removal of BTEX (benzene, toluene, ethyl benzene, as well as m, p-xylene and o-xylene) and confirmed biodegradation mechanism to be mainly responsible for benzene removal in the studied system (Mustafa et al. 2018).

In the search for green approaches toward sustainable development, emerging technologies based on nanoparticles or nanomaterials are now finding path to biodegradation application, which is improved owing to increased adsorption of substrates by nanomaterials, thanks to their larger surface/volume ratio. Nzila (Nzila 2018) reported the testing of this approach under aerobic and methanogenic (anaerobic) biodegradation. Bavandi et al. (2019) evaluated the removal efficiency of trinitrophenol by complementing carbon-based nanostructures with various types of metal nanoparticles along with microorganisms in a bubble column bioreactor. Removal efficiencies exceeding 90% for an initial trinitophenol concentration of 1301 mg/L were achieved.

In light of the fact that biodegradation is essentially a chain of enzyme-catalyzed reactions, the enzymatic method has evolved as one of the proposed treatment processes. Potent enzymes may be obtained from active microorganisms and immobilized for the direct application in IWW treatment. This biotechnique has emerged as a novel promising environmental-friendly and attractive sustainable alternative for the treatment of contaminated wastewaters. This topic is discussed thoroughly in a review by Demarche et al. (2012). A review article by Alshabib

(Alshabib and Onaizi 2019) was focused on comparing the advantages and drawbacks of both microbial (using living microorganisms) and enzymatic treatment and on reviewing recent advancement toward utilizing enzymes for phenolic wastewater treatment. Another study by Jun et al. (2019) highlighted the progress achieved on the dye and phenol removal practices using immobilized-enzyme treatment. Additionally, the study addressed the role and challenges of the nanotechnology as applied to enzyme immobilization. However, most of the enzymes reported in the literature for treatment of IWW are not yet commercially competitive, lending this technical and economic challenge for further research.

Biological reactors involve a multiple of operation modes, compound interactions, geometries, and hydraulic systems. The treatment of IWW has been focusing on employing conventional biofilm reactors such as fluidized bed bioreactors, fixed bed biofilm reactors, trickling bioreactors, microporous membranes, and combined anaerobic–aerobic bioreactors (Jou and Huang 2003; Quan et al. 2004; Kargi and Eker 2005; Kargi and Eker 2006). In parallel, it has also been exploring new types of bioreactors, which are practically robust and suitable for efficient long-term performance (El-Naas et al. 2010b). In this regard, novel reactors have been developed, which include the use of hollow fiber membrane contactors (Chung et al. 2005; Marrot et al. 2006; Juang and Wu 2007), microbial fuel cells (Luo et al. 2009; Huang et al. 2013; Kong et al. 2014), rotating rope bioreactors (Mudliar et al. 2008), pulsed plate bioreactors (Shetty et al. 2007; Shetty et al. 2011), and two-phase partitioning bioreactors (Cruickshank et al. 2000; Abu Hamed et al. 2004; Zhao et al. 2009). However, the practical utilization of most of these reactors in a full-scale industrial process is limited due to difficulties in long-term operation and scaling up (El-Naas et al. 2010b). Discussion on reactor types, performance, and design aspects can be found elsewhere (Al-Khalid and El-Naas 2012). The anaerobic baffled reactor (ABR) is essentially a series of up-flow anaerobic sludge blanket (UASB) reactors separated by baffles. Mahdavianpour et.al. (Mahdavianpour et al. 2018) developed a baffled react to treat wastewater with a high load of p-cresol. The effects of different operational parameters mainly p-cresol initial concentration and hydraulic retention time (HRT) on biodegradation of p-cresol and COD removal were investigated. Complete degradation of 1000 mg/L p-cresol could be attained at HRT of 24 h.

Rana et al. (2018) pointed out that conventional biological reactors have some inherent drawbacks such as poor mixing of liquid and poor oxygen transfer, which necessitate a need to modify novel bioreactors which can tackle these issues. A rotating biological contactor (RBC) is a fixed film biological treatment run in aerobic and anaerobic modes. It is preferred for its simple and cheap design, process stability, and eco-friendly operation. Also, it has the benefit of good contact between the microbial species and contaminant, thanks to the high interfacial area generated in the rotating disc. The RBC was subject to an optimization study for the treatment of synthetic phenolic wastewater. The process was proved to be efficient for treating high-strength organic wastewater.

In the context of green technologies, a synergetic integration exists between algae-based biorefineries and wastewaters/renewable energy systems. Algae cultivation bioreactor is used as an integral part of the wastewater treatment process, generating bioenergy at the same time. This was discussed in a review by Sadhukhan et al. (2018). The same objective of coupling wastewater treatment with the cultivation of microalgae for the generation of bioenergy was also investigated by Surkatti and Al-Zuhair (Surkatti and Al-Zuhair 2018) for the treatment of cresols. It was shown that Chlorella sp. can degrade p-cresol at a concentration up to 330 mg/L and use it for biomass growth. The overall process would be very attractive and economically feasible.

10.3 Combined or Integrated Methods in Industrial Wastewater Treatment

Nowadays, world economies face a major challenge in regard to commitment to long-term policies aimed at increasing and promoting sustainable, integrated, and balanced development. In response to this challenge, it is mandatory to implement best available scientific knowledge and innovative practices, aligned with continual re-evaluation of the development plans in light of the scientific updates (Urbaniec et al. 2018). Considering the complexity of waste and stringent environmental legislation, the main challenge to any industry is to manage the massive quantities of waste produced from diverse process streams (Srikanth et al. 2018).

As was pointed out in previous sections, the majority of IWW treatments are suitable for specific types of contaminants but may be inconvenient to others. Thus, there is an urgent need for a combination scheme of different treatments for enhanced removal efficiency in the overall treatment process. For example, if membranes are the only used method, then there would be the critical issue of fouling due to the presence of oils, solids, and bacteria. Consequently, pretreatment is required prior to the use of membranes. In an RO process, an acidification pretreatment would be useful to remove low molecular weight organic and inorganic materials and a post-treatment, such as softening, may also be needed (Jiménez et al. 2018). Therefore, the development of integrated processes for the management of IWW is strongly recommended. Physio-chemical and biological treatment processes should be combined and used to achieve different treatment goals. The choice of a suitable scheme is guided by criteria including cost of treatment and its intended purpose (reuse or discharge) as well as pertinent environmental standards. For example, a combination of coagulation, flotation, and filtration may be employed. According to Garcia-Segura et al. (2018), the purpose of integration is served irrespective of the sequence of the process in the integrated treatment matrix; it can be a combination of technologies into a reaction vessel or single treatment train.

AOPs have a recognized record of a successful application to reduce the concentrations of toxic organic pollutants that are resistant to degradation by biological treatment (Jiménez et al. 2018). Raslanigam et al. (2014) emphasized the combination of biological treatment with chemical oxidation with ozone (ozonation) as an effective process for decontamination of wastewater, to enhance the biodegradability of organic pollutants. Enhanced removal of phenol and chlorinated phenols was obtained by the combined process (Al-Khalid and El-Naas 2018). Bahri et al. (2018) presented a review on integrated oxidation process and biological treatment. A bio-electrochemical system was set as an example of an innovative approach that links bioenergy generation and wastewater treatment (Srikanth et al. 2018). In addition, adsorption and biodegradation processes have long been recognized for an effective combination by many researchers (Ma et al. 2013; El-Naas et al. 2014a). Sivagami et al. (2019) proposed an AOP combining ultrasound and Fenton's process for the treatment of total petroleum hydrocarbons (TPH) present in oil spill sludge. The combined process was successfully validated for the degradation of petroleum oil spill sludge.

Adsorptive removal and photocatalytic degradation of persistent organic pollutants in water have attracted considerable attention as energy- and cost-effective treatment methods. Pi et al. (2018) discussed the integration of adsorption and photocatalysis using metal-organic frameworks (MOF) as a recently developed class of multilateral porous materials, which have shown promising potential in adsorptive removal and photocatalytic degradation of persistent organic pollutants. MOFs aimed at addressing the issues related to the application of conventional adsorbents and photocatalysis for IWW treatment, such as limited surface area and porosity, low stability and reusability, and low conversion of solar energy.

The catalytic wet air oxidation (CWAO) process is becoming a well-known treatment of different industrial effluents with toxic and biorefractory organic wastes. This process is based on the concept of using oxygen for oxidizing the organic material in an aqueous phase at the operating conditions of 100–350 °C and 4.93–197.38 atm of reaction temperature and pressure, respectively. In a study by Al-Obaidi et al. (2018c), the two processes, CWAO and RO, were combined to provide the hybrid process. Reported advantages include promoted quality of treated water, reduced production cost, reduced energy consumption, and environmental compliance.

In a lab-scale study, a hybrid anaerobic-anoxic-oxic (A1/A2/O) process, involving both biofilm and suspended biomass, was applied to treat raw coke wastewater with high concentrations of polycyclic aromatic hydrocarbons (PAH) and operated more than 600 days. The process was optimized for organics and nitrogen removal by adjusting the operational conditions of total HRT and internally mixed liquor recirculation ratio from oxic reactor to anoxic reactor. In comparison with the conventional A1/A2/O system, a hybrid process can enhance the biodiversity in the system and thus improve the biodegradation of hazardous organics. The proposed hybrid A1/A2/O process was proven to be efficient and reliable for organics and nitrogen reduction whereas the total PAH concentration in the final effluent was substantially reduced due to the high removal efficiency (99%). However, the disposal of excess sludge should be addressed with special attention (Zhao et al. 2018).

A summary of the advantages and drawbacks of current treatment options was presented by Al-Khalid and El-Naas (2018). Biological treatment methods are cost-effective, eco-friendly, easy to handle, and involve direct degradation of pollutant compared to other treatment methods. Accordingly, the following section will be devoted to combined physio-chemical and microbiological processes.

10.3.1 Combined Chemical and Biological Systems

The combination of chemical and biological treatment approaches may result in a full treatment process to meet reuse and discharge water standards. The role of a chemical-biological treatment system is to perform oxidization or coagulation. Several chemical treatment processes were coupled with biological treatment including advanced oxidation processes, chemical coagulation, electrocoagulation, and ozonation and resulted in an effective integrated process for the treatment of several wastewater streams. Table 10.1 summarizes the combined chemical and biological processes for the treatment of different wastewater streams.

10.3.1.1 Photo-catalytic or Fenton Oxidation with Biological Treatment

Treatment of wastewater with a high concentration of organic pollutants using combined chemical oxidation and biological treatment has become a successful alternative to conventional methods. The application of the integrated system of chemical oxidation and biological reactor results in an efficient and cost-effective process. However, each process can be affected by different parameters. Chemical oxidation is usually affected by the reaction rate between organic substance and oxidants, amount of organics, and pH (Marco et al. 1997). Biological treatment is affected by a number of parameters such as temperature, pH, and contaminant concentration (Surkatti and El-Naas 2014). Thus, all these parameters must be arranged to end up with the optimum set-up for the combined chemical oxidation-biological process. In the chemical-biological oxidation, chemical oxidation offers moderate transformation of the organics using chemical means into an easily degradable product that can be subsequently degraded by using biological treatment into CO_2 and H_2O (Javier Benitez et al. 2001).

The application of the chemical oxidation process as a pretreatment stage before the biological treatment was commonly studied. A combination of photocatalytic oxidation using nanoparticles and biological treatment by fungi was studied for the treatment of high strength olive mill wastewater with high toxicity, COD content, and phenols concentrations. The application of two different nanoparticles (TiO_2 and Fe_2O_3) as a catalyst in photocatalytic oxidation was applied as a pretreatment step to reduce the concentration of organic pollutants before introducing the water stream to the biological treatment. Compared to iron nanoparticles as catalyst, TiO_2 showed a

Table 10.1 Summary of chemical-biological processes for the treatment of different IWW streams

Wastewater	Initial concentration	Chemical treatment	Biological degradation	Biodegradability measurement	References
Olive mill	COD=34000 mg/l	Ozonation in batch system for 8 h at 20 °C	Acclimated activated sludge in batch reactors	85.6% COD removal.	Benitez et al. (1999)
Olive mill	COD=59900 mg/l	Batch ozonation for 8h at 20 °C	Anaerobic digestion using acclimated immobilized biomass	70% COD removal.	Benitez et al. (1997)
Olive mill	COD=20,000mg/l	Ozonation	Aerobic biological treatment at room temperature	An overall COD removal of 87%, with 21% removal by ozonation process, and 83% COD removal using biological treatment.	Lafi et al. (2009)
Dye	COD=500mg/l	Ozonation at room temperature	Batch biological reactors	Complete color removal and partial COD removal using ozonation.	Maria et al. (2010)
Pharmaceutical	COD=2000 mg/l DOC[a]=620 mg/l	Ozonation	Membrane bioreactor	COD removal ranging from 85% to 90%.	Laera et al. (2012)
Pharmaceutical	COD=2000 mg/l DOC= 620 mg/l	UV/H_2O_2 process	Membrane bioreactor	COD removal ranging from 85% to 90%.	Laera et al. (2012)
Industrial	Phenol=200mg/l	Photocatalytic degradation using UV-light and TiO_2	Activated sludge system under high salinity media of 50 mg/l	More than 98% phenol removal in 25 h treatment (biological treatment for 24 h and photocatalysis for 1h).	Amour et al. (2008)
Pharmaceutical	DOC=775mg/l COD=3420mg/l	Solar photo-Fenton treatment using H_2O_2	Immobilized biological reactor (IBR)	About 95% DOC removal using combined photo-Fenton and with 33% using Fenton oxidation and 62% using biological treatment.	Sirtori et al. (2009)

Olive mill	COD=45,000mg/l	UV/ozonation	Aerobic biological treatment at room temperature	An overall COD removal of 91%, with 29% removal by UV/ozonation process, and 87% COD removal using biological treatment.	Lafi et al. (2009)
Pharmaceutical	COD=34,400 mg/L	Electrocoagulation using aluminum electrodes	Anaerobic fixed film fixed bed reactor (AFFBR)	COD removal of 80–90% and BOD removal of 86–94%, at organic loading rates (OLRs) of 0.6–4.0Kg COD/m^{3}d at 2 days HRT.	Deshpande et al. (2010)
Oil refinery	COD=19,440mg/l TPH =10,200mg/l	Electrocoagulation using aluminum electrodes	Fixed film biological reactor	98% TPH and 95% COD removal using electro-biofilter.	Pérez et al. (2016)
Table olive industry	COD=1200mg/l	Chemical treatment using Fenton’s oxidation	Aerobic biological treatment using an *Aspergillus niger* strain in a bubble column bioreactor	70% COD and 85% phenols removed by biological treatment. Chemical oxidation increased the removal efficiency of phenols.	Kotsou et al. (2004)
Pharmaceutical	COD=900-7000mg/l	Fenton’s oxidation	Aerobic degradation in SBR	An overall COD was 98%.	Tekin et al. (2006)
Coking	COD=16,000-21,000 mg/l	Oxidation-reduction and coagulation using zero-valent iron (ZVI) process	Biofilm reactors	96.1% COD removal.	Lai et al. (2009)

[a] Dissolved organic carbon

higher reduction in the organic pollutants, since the pre-treatment using chemical treatment with $TiO_2/H_2O_2/UV$ achieved 14%, 43%, 31%, and 38% reductions in aromatics content, color, total phenolic content (TPC), and COD, respectively, and there was no toxicity reduction using this step. The combined biological-chemical oxidation process improved COD and phenols removal efficiencies and also reduced the toxicity of treated wastewater (Nogueira et al. 2015). Bressan et al. (2004) investigated the application of combined catalytic oxidation with biotechnology for the treatment of olive oil mill wastewater with COD concentration up to 100,000 mg/l and phenols concentration of 5000 mg/l. The chemical oxidation process using an iron catalyst and dilute hydrogen peroxide (35%) was integrated with aerobic degradation using yeast and fungi; the combined process resulted in 80–90% COD removal (Bressan et al. 2004). Alizadeh et al. (2013) compared the combination of membrane bioreactor (MBR) with electro-Fenton, electrocoagulation, and electro-Fenton-Fenton process. Results indicated that the application of electro-Fenton-Fenton oxidation with the MBR resulted in COD removal efficiency of 96.57% by the integrated electro-Fenton-Fenton MBR system.

The treatment of real pharmaceutical wastewater using combined advanced oxidation process and biological treatment was investigated by Sirtori et al. (2009). They applied Fenton oxidation as a pre-treatment step, followed by biotreatment using IBR. The wastewater was characterized with its high COD and dissolved organic carbon (DOC) contents and the combined process achieved more than 90% DOC reduction. Photocatalysis coupled with biological treatment process has proven to be an effective technique to treat phenolic wastewater. L'Amour et al. (2008) confirmed the efficiency of the combination of photocatalysis and biological treatment process using activated sludge in the degradation of phenols from wastewater under high salinity treatment conditions. The study resulted in 98% phenol removal from the wastewater stream within 24 h of biological treatment and 1 h of chemical treatment. The application of Fenton's oxidation as a pre-treatment step for the treatment of the pharmaceutical wastewater was also investigated by Tekin et al. (2006). The study illustrated the application of Fenton's oxidation using H_2O_2/Fe^{2+} followed by aerobic degradation using SBR for COD removal. Under optimum H_2O_2/Fe^{2+} ratio, Fenton's oxidation process achieved 45–60% COD removal, and it also increased the efficiency of the SBR up to 50%. However, the combined chemical-biological treatment resulted in a 98% COD reduction (Tekin et al. 2006). Kotsou et al. (2004) studied the performance of the combination of aerobic biological treatment in a bubble column bioreactor using an *Aspergillus niger* with chemical oxidation, for the treatment of table olive industry. Biological treatment processes achieved 70% COD removal and 95% phenol reduction within 2 days. However, the application of chemical oxidation using Fenton's oxidation process enhanced the removal of residual phenols. Malato et al. (2007) studied the pilot scale application of combined chemical oxidation with biological treatment for the degradation of non-biodegradable organics in wastewater effluent. The Fenton oxidation was applied as a pre-treatment step before the biological treatment using immobilized biological reactor and used to treat wastewater characterized by high total organic carbon (TOC) content (500mg/l). The wastewater treatment plant demonstrated a highly efficient and cost-effective process.

10.3.1.2 Ozonation with Biological Treatment

Generally, ozonation is applied for water disinfection and it also has a high potential to be applied as a pretreatment step for highly contaminated IWW. The characteristic of ozone is that it is rather selective toward double bonds. Ozonation has main disadvantages including the formation of a by-product that may have a toxic and carcinogenic effect. Andreozzi et al. (1998) confirmed that coupling ozonation as chemical pretreatment with biological treatment showed high performance in reducing COD and polyphenols from high strength olive mill wastewater. Results showed that ozonation pre-treatment step has the ability to reduce 50% of total phenols; however, most of the COD reduction was obtained under the biological treatment step using anaerobic digestion. Benitez et al. (1999) also studied the application of ozonation as a pretreatment process before aerobic treatment of olive mill wastewater. Compared to single processes, the combined treatment process achieved higher COD and organic matter removal. De Souza et al. (2010) studied the combination of a chemical process (ozonation) and biological degradation with a biofilm. Ozonation treatment process achieved partial removal of COD and complete color removal from the wastewater effluent. The study concluded that pre-treatment using ozonation process resulted in the formation of more toxic effluents compared to the initial synthetic wastewater. Therefore, the application of the integrated ozonation process and biological treatment achieved the toxicity reduction in the stream and lead to complete mineralization of compounds. The application of ozonation as post-treatment was also investigated by a number of researchers. Lotito et al. (2012) studied the degradation of textile wastewater by applying a biological treatment process followed by ozonation. Results showed 60% COD reduction after the biological treatment step and the COD removal was enhanced by applying ozonation as a post-treatment step. The utilization of ozonation process as post-treatment was studied in a pilot scale by Schaar et al. (2010). The study investigated the addition of ozonation step after the biological treatment process of a real wastewater treatment plant (WWTP) for the removal of the residual organic pollutants present in the effluent stream after the biological treatment. Ozonation of WWTP effluent increased the efficiency of the treatment process.

Benitez et al. (2003) compared the performance of ozonation, activated sludge system, and combined ozonation-activated sludge system process for the treatment of industrial wastewater in a continuous process. Results showed that the combined process resulted in the highest COD removal (up to 89%), compared to ozonation and activated sludge system that achieved maximum removal of 54% and 81%, respectively. Lafi et al. (2009) compared the application of ozonation and ozonation/UV oxidation with biological treatment as pre-treatment or post-treatment steps.

Results showed that the application of ozonation as a pre-treatment step before aerobic biodegradation achieved 87% COD removal. In contrast, lower COD removal (80%) resulted by the application of ozonation as a post-treatment process. However, the combination of UV/ozonation as a pre-treatment step achieved an overall COD removal of 90%.

10.3.1.3 Chemical and Electro-coagulation with Biological Treatment

Electrocoagulation is one of the most effective alternatives for the treatment of complex effluents such as petrochemical, refinery, and pharmaceutical wastewaters. The application of electrocoagulation with biological treatment has been developed for the treatment of oil refinery wastewater and compared with the electrocoagulation treatment process. The effluent was treated using electrocoagulation (EC) using aluminum electrodes followed by fixed film aerobic bioreactor under different operating conditions. Under the optimum conditions, the EC unit obtained an overall percentage removal of 88% and 80% for COD and TPH. However, the utilization of coupled EC-aerobic bioreactors increased the performance of wastewater treatment and resulted in 98% TPH and 95% COD removals in refinery wastewater treatment (Pérez et al. 2016). Bani-Melhem and Smith (Bani-melhem and Smith 2012) reported the application of an integrated process encompassing electrocoagulation (EC) and submerged membrane bioreactor (SMBR) units. The integrated system was compared with the SMBR process and showed that the EC-SMBR resulted in higher removal of COD from the effluent compared to SMBR. Vinduja and Balasubramanian (2013) studied several integrated systems consisting of electrocoagulation integrated with microfiltration, MBR, and membrane bioreactor integrated with electrocoagulation. Results showed that MBR integrated with electrocoagulation resulted in the best treatment performance and showed the highest COD and metal removal from the wastewater stream. Deshpande et al. (2010) investigated the pharmaceutical wastewater treatment using a combined treatment process that comprises electrocoagulation cell for pretreatment step followed by AFFBR. Under optimum operation parameters, the electrocoagulation unit achieved COD and BOD removals of 24% and 35%, respectively. However, 80–90% COD and 86–94% BOD reductions were obtained using the combined chemical-biological treatment process. These results illustrated that the combined treatment system option is competitive and can be applied effectively for high strength wastewaters.

10.3.2 Physical-Biological Treatment

The application of physical-biological wastewater treatment was developed a long time ago, during the 1970s; a combination of suspended growth biological reactor and membrane ultrafiltration unit as wastewater treatment system was utilized for the treatment of organic pollutants from wastewater. Sutton et al. (1994) then developed a pilot plant for a physical-biological treatment system which consisted of a membrane bioreactor combined with a membrane ultrafiltration unit. The system was tested for the treatment of real industrial oily wastewater over several months. Although the wastewater treatment plant faced minor process and mechanical problems during start-up, the pilot plant was successfully operated under stable conditions for two months and achieved more than 90% COD removal. Wang et al. (2016) compared the performance of activated sludge system (AS), powdered activated carbon (PAC), and integrated activated sludge-powdered activated carbon system (AS-PAC) in the treatment of chemical IWW. Compared to a single treatment process, the addition of powdered activated carbon to the biological system (AS-PAC) resulted in highest total organic carbon and organic matters of 64.4% and 68.1%, respectively. Beccari et al. (1999) compared the several physical treatment methods as a pretreatment step prior to the biological treatment for the treatment of olive mill wastewater. Sedimentation, centrifugation, filtration, and ultrafiltration were compared as physical treatment processes. Results showed that ultrafiltration unit achieved the highest COD removal (65.1%) and polyphenols (60%) as a pretreatment step before the application of anaerobic biological treatment. Di Bella et al. (2008) developed a mathematical model for a membrane bioreactor that performs physical and biological treatment simultaneously. The model is divided into two sub-models, one for the biological process carried out in biological membrane and the other for the physical feature running in membrane filtration. The model was applied in a suspended media biological reactor and tested for the treatment of raw WWTP effluent for a period of 130 days. The developed model proved to be a useful tool in optimizing wastewater treatment parameters to achieve high COD and total suspended solids (TSS) removal. Sahinkaya et al. (2008) applied a biological-physical wastewater treatment system which involves an activated sludge treatment process coupled with nanofiltration process as post-treatment stage, for textile wastewater treatment. The application of activated sludge process resulted in total COD removal and color removal of 91% and 75%, respectively. In order to achieve treated wastewater with higher quality for reuse purposes, nanofiltration was applied as a polishing step and resulted in complete removal of color and COD.

10.3.3 Three-Step Integrated System

In the area of wastewater treatment, the combination of biological treatment with physical and chemical treatment is needed to handle high strength wastewater effluents, such as refinery, textile, and petrochemical industries wastewater. Although biological treatment is proven to be effective in the removal of several organic compounds from IWW, biological treatment of heavily contaminated wastewater cannot be effective as a single unit. Thus, to achieve complete removal of organic pollutants, it is necessary to combine biological treatment methods with other physiochemical and mechanical treatment methods. Ahn et al. (1999) developed an integrated system that consisted of Fenton's oxidation and activated carbon adsorption as a pre-treatment step followed by a fixed bed biofilm process. The system was investigated for the treatment of dyestuff wastewater having high organics concentrations. Fenton's oxidation process reduced the COD concentration from 9200 to 2460 mg/l (74.9%) and complete COD removal resulted from the combined process. The study showed that the application of Fenton's oxidation and a carbon adsorption process is an effective pre-treatment step to improve the biological treatment and reduce the cost of the overall process (Ahn et al. 1999). Turan-Ertas (Turan-Ertas 2001) compared a physical-chemical system with the application of a biological-chemical system for the removal of color and organic compounds from dye wastewater. A combined system of ozonation-chemical clarification was compared with ozonation-biological treatment process for the removal of color and medium strength wastewater. Maximum COD removal efficiencies up to 71% and 82%, respectively, were achieved. A combination of ozonation and biological treatment can be applied for the treatment of medium strength wastewater to obtain an efficient color and COD removal. However, chemical clarification is required as a pre-treatment step before ozonation-biological treatment, for the treatment of high strength dye wastewater. De Gisi et al. (2009) investigated the use of the biological treatment as a pre-treatment step before the physiochemical treatment process for the treatment of tannery wastewater that contains high COD content ranging from 2000 to 7600 mg/l, in addition to other contaminants including ammonium substances, organic compounds, salts, and sulfur. Activated sludge system as pre-treatment stage achieved 67% COD reduction and low percentage ammonia removal. The main treatment step comprised RO unit with a plane membrane; it showed high performance in achieving COD removal of 97.4%. However, the percentage removal of ammonia and nitrate are 96.1% and 98.5%, respectively. Beccari et al. (1999) suggested the application of a physical-chemical process as a pre-treatment step before the bioprocess for the treatment of olive mill wastewater. The application of centrifugation and chemical addition such as calcium salt and bentonite before the biological process resulted in the maximum removal efficiency.

Biological treatment has been applied as a pre-treatment step for the reduction of COD and color from textile wastewater. Kim et al. (2003) investigated the performance of a combined system consisting of biological treatment–chemical coagulation–chemical oxidation in the decolonization and reduction of COD in lab-scale and pilot plant. Results concluded that biological treatment using microorganisms in support materials (pre-treatment step) resulted in 69% COD reduction, however the COD removal percentages reached 94% after chemical coagulation and chemical oxidation as second and third stages had been incorporated. Reungoat et al. (2012) investigated the removal of organic chemicals in three full-scale plants consisting of ozonation and biological activated carbon (BAC) filtration to treat WWTP effluents. Low DOC removal (<10%) was obtained after the ozonation step, the following step of BAC achieved between 20% and 50% DOC removal. However, the filtration step achieved the complete removal of the residual DOC.

The application of chemical-biological-physical treatment was investigated in both lab and pilot scale. A lab scale combined process of chemical, biological, and physical treatment was developed for the removal of phenol and acids from pharmaceutical wastewater. The integrated process consisting of pre-ozonation and advanced treatment step of moving bed BAC was developed for the treatment of highly organics-contaminated IWW, with high COD, and high phenol of 1260 and 10,000 mg/l, respectively. Results showed that the pre-treatment step resulted in significant reduction in the COD concentration, however the integrated system achieved up to 95% removal (Lin et al. 2001). El-Naas et al. (2014a) have also developed chemical-biological-physical treatment of refinery wastewater with high COD. The three-step integrated system was composed of EC as pre-treatment step, then biological treatment using immobilized aerobic bacteria in SBBR, followed by adsorption (AD) using activated carbon as post-treatment step; it was used for the removal of phenols and COD. Results showed that only 18% phenol removal and more than 50% COD removal were obtained using electrocoagulation unit, compared to 97% and 100% COD and phenol reduction, respectively, resulted by the combined EC-SBBR-AD treatment process. A similar system was applied by El-Naas et al. (2016) for the treatment of real refinery wastewater in a full-scale pilot plant. The integrated EC-SBBR-AD process was designed, fabricated, and tested for real refinery wastewater treatment for a period of 10 months using flow rate of 1 m^3/h and operated continuously for 12 h. The pilot plant resulted in complete removal of phenols and 96% COD removal.

A comparison of several integrated systems was reported by Nawaz and Ahsan (2014) for textile wastewater with COD concentration of 433 mg/l and TSS of 244 mg/l. About 57.5% COD reduction was achieved using conventional activated sludge as a pre-treatment step. However, the combined process of biological treatment using activated sludge system followed by sand filtration and adsorption using activated carbon as polishing steps resulted in the higher removal efficiency of 81.6% organics, 88.5% TSS, and 94.5% color. It should be mentioned that most of the real wastewater treatment plants are more complicated and may consist of four or five treatment steps. A case study of real refinery wastewater treatment was conducted using four-stage wastewater treatment system. The system started with a pre-treatment step consisting of American Petroleum Institute (API), primary oil water gravity separators, and parallel-plates-interceptors; then a physiochemical treatment step comprising neutralization, coagulation, and flotation; followed by a biological treatment process using conventional activated sludge system; and finally an advanced treatment step that involves clarification, chlorination, mechanical aeration, and filtration. The integrated system resulted in treated wastewater with high standards and achieved more than 90% removal efficiencies for phenols, sulfides, oil and grease, volatile suspended solids (VSS), TSS, and TPH. However, 80–90% removal was obtained for COD, BOD, and total nitrogen and chloride was removed with around 60% removal. Therefore, the four-stage WWTP presented a full treatment system that operated with high efficiency and low cost to produce treated wastewater with high quality for discharge or reuse (Santos et al. 2015). Table 10.2 presents a summary of integrated three-step system for the treatment of IWW.

Table 10.2 Integrated three-step wastewater treatment systems

Type	Pre-treatment	Secondary step	Post-treatment	Scale	IWW	Performance	References
Chemical-biological-physical	Electrocoagulation using aluminum electrode current density of 3 mA/cm^2	SBBR using *Pseudomonas putida* immobilized in PVA gel at 30 °C	Adsorption using activated carbon with mass of 130g at room temperature	Lab	Refinery	97% COD removal 100% phenol removal	El-Naas et al. (2014a)
Chemical-chemical-biological	Ozonation in semi-continuous mode	Flocculation by slow mixing followed, by sedimentation and coagulation	Two-batch activated sludge reactors using 2L	Lab	Dye	—	Turan-Ertas (2001)
Biological-physical-physical	Activated sludge in SBR	Sand filtration	Activated carbon adsorption	Lab	Textile	86.1% organics 88.1% TSS reduction	Nawaz and Ahsan (2014)
Chemical-physical-biological	Fenton's oxidation with dosing concentration (mg/l) H_2O_2:$FeSO_4 \cdot 7H_2O$ of 700:3500	Adsorption using activated carbon	Fixed bed reactor	Lab	Dyestuff	100% COD removal	Ahn et al. (1999)
Chemical-biological-physical	Electrocoagulation unit with multiple electrodes with maximum capacity of 1.48 m^3/l and current of 65A	SBBR using *Pseudomonas putida* immobilized in PVA gel operation volume 1 m^3, temperature 30–35 °C, and pH 7–7.5	Adsorption using two parallel columns; each is packed with 250 kg of GAC[a], with total bed volume of 0.5 m^3	Pilot	Refinery	96% COD and 100% phenol removal	El-Naas et al. (2016)
Chemical-physical and biological	Ozonation	Moving-bed BAC	Activated carbon	Lab	Petrochemical industry	85–95% COD reduction	Lin et al. (2001)
Biological-chemical-chemical	Biological treatment	Chemical coagulation	Electrochemical oxidation	Pilot scale	Textile	95.4% COD reduction and 98.5% color removal	Kim et al. (2003)

[a] Granular activated carbon

References

Abdelwahab O, Amin NK, El-Ashtoukhy ESZ (2009) Electrochemical removal of phenol from oil refinery wastewater. J Hazard Mater. 163(2–3):711–716

Abu Bakar SNH, Abu Hasan H, Mohammad AW, Sheikh Abdullah SR, Haan TY, Ngteni R, et al (2018) A review of moving-bed biofilm reactor technology for palm oil mill effluent treatment. J Clean Prod [Internet] 171:1532–1545. Available from: https://doi.org/10.1016/j.jclepro.2017.10.100

Abu Hamed T, Bayraktar E, Mehmetoğlu Ü, Mehmetoğlu T (2004) The biodegradation of benzene, toluene and phenol in a two-phase system. Biochem Eng J 19(2):137–146

Ahmad ZU, Yao L, Wang J, Gang DD, Islam F, Lian Q, et al. (2019) Neodymium embedded ordered mesoporous carbon (OMC) for enhanced adsorption of sunset yellow: characterizations, adsorption study and adsorption mechanism. Chem Eng J [Internet] 359(September 2018):814–826. Available from: https://doi.org/10.1016/j.cej.2018.11.174

Ahn DH, Chang WS, Yoon T II (1999) Dyestuff wastewater treatment using chemical oxidation, physical adsorption and fixed bed biofilm process. Process Biochem 34(5):429–439

Al-Ghouti MA, Al-Kaabi MA, Ashfaq MY, Da'na DA (2018) Produced water characteristics, treatment and reuse: a review. J Water Process Eng [Internet] 28(September 2018):222–239. Available from: https://doi.org/10.1016/j.jwpe.2019.02.001

Alias NH, Jaafar J, Samitsu S, Matsuura T, Ismail AF, Othman MHD, et al (2019) Photocatalytic nanofiber-coated alumina hollow fiber membranes for highly efficient oilfield produced water treatment. Chem Eng J [Internet] 360(October 2018):1437–1446. Available from: https://doi.org/10.1016/j.cej.2018.10.217

Alizadeh M, Aminzadeh B, Taheri M, Farhadi S (2013) MBR excess sludge reduction by combination of electrocoagulation and Fenton oxidation processes. Sep Purif Technol [Internet] 120:378–385. Available from: https://doi.org/10.1016/j.seppur.2013.10.012

Al-Khalid T, El-Naas MH (2012) Aerobic biodegradation of phenols: a comprehensive review. Crit Rev Environ Sci Technol 42(16):1631–1690

Al-Khalid T, El-Naas M (2018) Organic contaminants in refinery wastewater: characterization and novel approaches for biotreatment. In: Intechopen, pp 371–391

Al-Obaidi MA, Kara-Zaïtri C, Mujtaba IM (2018a) Simulation and optimisation of a two-stage/two-pass reverse osmosis system for improved removal of chlorophenol from wastewater. J Water Process Eng [Internet] 22(February):131–137. Available from: https://doi.org/10.1016/j.jwpe.2018.01.012

Al-Obaidi MA, Kara-Zaïtri C, Mujtaba IM (2018b) Simulation and optimisation of a two-stage/two-pass reverse osmosis system for improved removal of chlorophenol from wastewater. J Water Process Eng [Internet] 22(November 2017):131–137. Available from: https://doi.org/10.1016/j.jwpe.2018.01.012

Al-Obaidi MA, Jarullah AT, Kara-Zaïtri C, Mujtaba IM (2018c) Simulation of hybrid trickle bed reactor–reverse osmosis process for the removal of phenol from wastewater. Comput Chem Eng [Internet] 113:264–273. Available from: https://doi.org/10.1016/j.compchemeng.2018.03.016

Alshabib M, Onaizi SA (2018) A review on phenolic wastewater remediation using homogeneous and heterogeneous enzymatic processes: current status and potential challenges. Sep Purif Technol [Internet] 219(October 2018):186–207. Available from: https://doi.org/10.1016/j.seppur.2019.03.028

Andreozzi R, Longo G, Majone M, Modesti G (1998) Integrated treatment of olive oil mill effluents (OME): study of ozonation coupled with anaerobic digestion. Water Res 32(8):2357–2364

Anis SF, Hashaikeh R, Hilal N (2019) Reverse osmosis pretreatment technologies and future trends: a comprehensive review. Desalination [Internet] 452(October 2018):159–195. Available from: https://doi.org/10.1016/j.desal.2018.11.006

Bahri M, Mahdavi A, Mirzaei A, Mansouri A, Haghighat F (2018) Integrated oxidation process and biological treatment for highly concentrated petrochemical effluents: a review. Chem Eng

Process - Process Intensif [Internet] 125(August 2017):183–196. Available from: https://doi.org/10.1016/j.cep.2018.02.002

Bani-melhem K, Smith E (2012) Grey water treatment by a continuous process of an electrocoagulation unit and a submerged membrane bioreactor system. Chem Eng J [Internet] 198–199:201–210. Available from: https://doi.org/10.1016/j.cej.2012.05.065

Basak B, Jeon BH, Kurade MB, Saratale GD, Bhunia B, Chatterjee PK, et al (2019) Biodegradation of high concentration phenol using sugarcane bagasse immobilized Candida tropicalis PHB5 in a packed-bed column reactor. Ecotoxicol Environ Saf [Internet] 180(May):317–325. Available from: https://doi.org/10.1016/j.ecoenv.2019.05.020

Bavandi R, Emtyazjoo M, Saravi HN, Yazdian F, Sheikhpour M (2019) Study of capability of nanostructured zero-valent iron and graphene oxide for bioremoval of trinitrophenol from wastewater in a bubble column bioreactor. Electron J Biotechnol [Internet] 39:8–14. Available from: https://doi.org/10.1016/j.ejbt.2019.02.003

Beccari M, Majone M, Riccardi C, Savarese F, Torrisi L (1999) Integrated treatment of olive oil mill effluents effect of chemical and physical pretreatment on anaerobic treatability. Water Sci Technol 40(1):347–355

Bel Hadjltaief H, Sdiri A, Ltaief W, Da Costa P, Gálvez ME, Ben Zina M (2018) Efficient removal of cadmium and 2-chlorophenol in aqueous systems by natural clay: adsorption and photo-Fenton degradation processes. Comptes Rendus Chim 21(3–4):253–262

Benitez FJ, Torregrosa J, Acero JL (1997) Improvement of the anaerobic biodegradation of olive mill wastewaters by prior ozonation pretreatment. Bioprocess Eng 17:169–175

Benitez FJ, Beltran-heredia J, Torregrosa J, Acero JL (1999) Treatment of olive mill wastewaters by ozonation, aerobic degradation and the combination of both treatments. J Chem Technol Biotechnol 646(February):639–646

Benitez FJ, Acero JL, Garcia J, Leal AI (2003) Purification of cork processing wastewaters by ozone, by activated sludge, and by their two sequential applications. Water Res 37:4081–4090

Bressan M, Liberatore L, D'Alessandro N, Tonucci L, Belli C, Ranalli G (2004) Improved combined chemical and biological treatments of olive oil mill wastewaters. J Agric Food Chem 52(5):1228–1233

Chung TP, Wu PC, Juang RS (2005) Use of microporous hollow fibers for improved biodegradation of high-strength phenol solutions. J Memb Sci 258(1–2):55–63

Cruickshank SM, Daugulis AJ, McLellan PJ (2000) Modelling of a continuous two-phase partitioning bioreactor for the degradation of xenobiotics. Process Biochem 35(9):1027–1035

De Gisi S, Galasso M, De Feo G (2009) Treatment of tannery wastewater through the combination of a conventional activated sludge process and reverse osmosis with a plane membrane. Desalination [Internet] 249(1):337–342. Available from: https://doi.org/10.1016/j.desal.2009.03.014

Demarche P, Junghanns C, Nair RR, Agathos SN (2012) Harnessing the power of enzymes for environmental stewardship. Biotechnol Adv [Internet] 30(5):933–953. Available from: https://doi.org/10.1016/j.biotechadv.2011.05.013

Dermeche S, Nadour M, Larroche C, Moulti-Mati F, Michaud P (2013) Olive mill wastes: Biochemical characterizations and valorization strategies. Process Biochem [Internet] 48(10):1532–1552. Available from: https://doi.org/10.1016/j.procbio.2013.07.010

Deshpande AM, Satyanarayan S, Ramakant S (2010) Treatment of high-strength pharmaceutical wastewater by electrocoagulation combined with anaerobic process. Water Sci Technol 61(2):463–472

Di Bella G, Mannina G, Viviani G (2008) An integrated model for physical-biological wastewater organic removal in a submerged membrane bioreactor: model development and parameter estimation. J Memb Sci 322:1–12

Diya'Uddeen BH, Daud WMAW, Abdul Aziz AR (2011) Treatment technologies for petroleum refinery effluents: a review. Process Saf Environ Prot 89(2):95–105

El-Naas MH, Al-Zuhair S, Al-Lobaney A, Makhlouf S (2009) Assessment of electrocoagulation for the treatment of petroleum refinery wastewater. J Environ Manage [Internet] 91(1):180–185. Available from: https://doi.org/10.1016/j.jenvman.2009.08.003

El-Naas MH, Al-Zuhair S, Alhaija MA (2010a) Removal of phenol from petroleum refinery wastewater through adsorption on date-pit activated carbon. Chem Eng J [Internet] 162(3):997–1005. Available from: https://doi.org/10.1016/j.cej.2010.07.007

El-Naas MH, Al-Zuhair S, Makhlouf S (2010b) Continuous biodegradation of phenol in a spouted bed bioreactor (SBBR). Chem Eng J 160(2):565–570

El-Naas MH, Alhaija MA, Al-Zuhair S (2014a) Evaluation of a three-step process for the treatment of petroleum refinery wastewater. J Environ Chem Eng [Internet] 2(1):56–62. Available from: https://doi.org/10.1016/j.jece.2013.11.024

El-Naas MH, Surkatti R, Al-Zuhair S (2014b) Petroleum refinery wastewater treatment: A pilot scale study. J Water Process Eng [Internet] 14:71–76. Available from: https://doi.org/10.1016/j.jwpe.2016.10.005

Garcia-Segura S, Ocon JD, Chong MN (2018) Electrochemical oxidation remediation of real wastewater effluents — a review. Process Saf Environ Prot [Internet] 113:48–67. Available from: https://doi.org/10.1016/j.psep.2017.09.014

Gautam A, Rawat S, Verma L, Singh J, Sikarwar S, Yadav BC, et al (2018) Green synthesis of iron nanoparticle from extract of waste tea: An application for phenol red removal from aqueous solution. Environ Nanotechnology, Monit Manag [Internet] 10(August):377–387. Available from: https://doi.org/10.1016/j.enmm.2018.08.003

Ghobashy MM, Younis SA, Elhady MA, Serp P (2018) Radiation induced in-situ cationic polymerization of polystyrene organogel for selective absorption of cholorophenols from petrochemical wastewater. J Environ Manage [Internet] 210:307–315. Available from: https://doi.org/10.1016/j.jenvman.2018.01.018

Hassan H, Jin B, Donner E, Vasileiadis S, Saint C, Dai S(2018) Microbial community and bioelectrochemical activities in MFC for degrading phenol and producing electricity: microbial consortia could make differences. Chem Eng J [Internet] 332(September 2017):647–657. Available from: https://doi.org/10.1016/j.cej.2017.09.114

Huang L, Sun Y, Liu Y, Wang N (2013) Mineralization of 4-chlorophenol and analysis of bacterial community in microbial fuel cells. Procedia Environ Sci [Internet] 18:534–539. Available from: https://doi.org/10.1016/j.proenv.2013.04.072

Javier Benitez F, Acero JL, Gonzalez T, Garcia J (2001) Organic matter removal from wastewaters of the black olive industry by chemical and biological procedures. Process Biochem 37(3):257–265

Jiménez S, Micó MM, Arnaldos M, Medina F, Contreras S (2018) State of the art of produced water treatment. Chemosphere 192:186–208

Jou CG, Huang G (2003) A pilot study for oil refinery wastewater treatment using a fixed-film bioreactor. Adv Environ Res 7:463–469

Juang RS, Wu CY (2007) Microbial degradation of phenol in high-salinity solutions in suspensions and hollow fiber membrane contactors. Chemosphere 66(1):191–198

Jun LY, Yon LS, Mubarak NM, Bing CH, Pan S, Danquah MK, et al (2019) An overview of immobilized enzyme technologies for dye and phenolic removal from wastewater. J Environ Chem Eng [Internet] 7(2):102961. Available from: https://doi.org/10.1016/j.jece.2019.102961

Kargi F, Eker S (2005) Removal of 2,4-dichlorophenol and toxicity from synthetic wastewater in a rotating perforated tube biofilm reactor. Process Biochem 40(6):2105–2111

Kargi F, Eker S (2006) Effect of sludge age on performance of an activated sludge unit treating 2,4 dichlorophenol-containing synthetic wastewater. Enzyme Microb Technol 38(1–2):60–64

Khan MZ, Mondal PK, Sabir S (2013) Aerobic granulation for wastewater bioremediation: a review. Can J Chem Eng 91(6):1045–1058

Kim S, Park C, Kim T-H, Lee J, Kim S-W (2003) COD reduction and decolorization of textile effluent using a combined process. J Biosci Bioeng. 95(1):102–105

Kong F, Wang A, Ren HY, Huang L, Xu M, Tao H (2014) Improved dechlorination and mineralization of 4-chlorophenol in a sequential biocathode-bioanode bioelectrochemical system with mixed photosynthetic bacteria. Bioresour Technol [Internet] 158:32–38. Available from: https://doi.org/10.1016/j.biortech.2014.01.142

Kotsou M, Kyriacou A, Lasaridi K, Pilidis G (2004) Integrated aerobic biological treatment and chemical oxidation with Fenton' s reagent for the processing of green table olive wastewater. Semantic Scholar 39:1653–1660

L'Amour L, Bessa E, Gomes S, Leite F (2008) Removal of phenol in high salinity media by a hybrid process (activated sludge + photocatalysis). Semantic Scholar 60:142–146

Laera G, Cassano D, Lopez A, Pinto A, Pollice A, Ricco G et al (2012) Removal of organics and degradation products from industrial wastewater by a membrane bioreactor integrated with ozone or UV/H 2O 2 treatment. Environ Sci Technol 46(2):1010–1018

Lafi WK, Shannak B, Al-shannag M, Al-anber Z, Al-hasan M (2009) Treatment of olive mill wastewater by combined advanced oxidation and biodegradation. 70:141–146

Lai P, Zhao H, Zeng M, Ni J (2009) Study on treatment of coking wastewater by biofilm reactors combined with zero-valent iron process. Semantic Scholar 162:1423–1429

Li B, Sun Y, Li Y (2005) Pretreatment of coking wastewater using anaerobic sequencing batch reactor (ASBR). J Zhejiang Univ Sci B [Internet]. 6(11):1115–1123. Available from: http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=1390660&tool=pmcentrez&rendertype=abstract

Liao Y, Goh S, Tian M, Wang R, Fane AG (2018) Design, development and evaluation of nanofibrous composite membranes with opposing membrane wetting properties for extractive membrane bioreactors. J Memb Sci [Internet] 551(December 2017):55–65. Available from: https://doi.org/10.1016/j.memsci.2018.01.029

Lin C, Tsai T, Liu J, Chen M (2001) Enhanced biodegradation of petrochemical wastewater using ozonation and bac advanced treatment system. Water Res 35(3):699–704

Liu X, Wu S, Zhang D, Shen J, Han W, Sun X, et al (2018a) Simultaneous pyridine biodegradation and nitrogen removal in an aerobic granular system. J Environ Sci (China) [Internet] 67:318–329. Available from: https://doi.org/10.1016/j.jes.2017.09.016

Liu SH, Chang CM, Lin CW (2018b) Modifying proton exchange membrane in a microbial fuel cell by adding clay mineral to improve electricity generation without reducing removal of toluene. Biochem Eng J [Internet] 134:101–107. Available from: https://doi.org/10.1016/j.bej.2018.03.013

Luo H, Liu G, Zhang R, Jin S (2009) Phenol degradation in microbial fuel cells. Chem Eng J 147(2–3):259–264

Ma X, Li N, Jiang J, Xu Q, Li H, Wang L, Lu J (2013) Adsorption–synergic biodegradation of high-concentrated phenolic water by Pseudomonas putida immobilized on activated carbon fiber. J Environ Chem Eng 1(3):466–472

Mahdavianpour M, Moussavi G, Farrokhi M (2018) Biodegradation and COD removal of p-Cresol in a denitrification baffled reactor: performance evaluation and microbial community. Process Biochem 69:153–160

Malato S, Maldonado MI, Oller I, Gernjak W, Leonidas P (2007) Coupling solar photo-Fenton and biotreatment at industrial scale: main results of a demonstration plant. J Hazard Mater 146:440–446

Marco A, Esplugas S, Saum G (1997) How and why combine biological and chemical treatment. Water Sci Technol 35(4):321–327

Maria S, Guelli DA, De SU, Angela K, Bonilla S, Augusto A et al (2010) Removal of COD and color from hydrolyzed textile azo dye by combined ozonation and biological treatment. J Hazard Mater 179:35–42

Maria A, Fratino U, Bergna G, Di C (2018) Integrated biological and ozone treatment of printing textile wastewater. Chem Eng J [Internet] 195–196:261–269. Available from: https://doi.org/10.1016/j.cej.2012.05.006

Marrot B, Barrios-Martinez A, Moulin P, Roche N (2006) Biodegradation of high phenol concentration by activated sludge in an immersed membrane bioreactor. Biochem Eng J 30(2):174–183

Martín J, Orta M del M, Medina-Carrasco S, Santos JL, Aparicio I, Alonso E (2018) Removal of priority and emerging pollutants from aqueous media by adsorption onto synthetic organo-funtionalized high-charge swelling micas. Environ Res [Internet] 164(March):488–494. Available from: https://doi.org/10.1016/j.envres.2018.03.037

Mudliar SN, Padoley KV, Bhatt P, Sureshkumar M, Lokhande SK, Pandey RA et al (2008) Pyridine biodegradation in a novel rotating rope bioreactor. Bioresour Technol 99(5):1044–1051

Mustafa A, Azim MK, Raza Z, Kori JA (2018) BTEX removal in a modified free water surface wetland. Chem Eng J [Internet] 333(September 2017):451–455. Available from: https://doi.org/10.1016/j.cej.2017.09.168

Nancharaiah Y V., Kiran Kumar Reddy G (2018) Aerobic granular sludge technology: Mechanisms of granulation and biotechnological applications. Bioresour Technol [Internet] 247 (September 2017):1128–1143. Available from: https://doi.org/10.1016/j.biortech.2017.09.131

Nawaz MS, Ahsan M (2014) Comparison of physico-chemical, advanced oxidation and biological techniques for the textile wastewater treatment. Alexandria Eng J [Internet] 53(3):717–722. Available from: https://doi.org/10.1016/j.aej.2014.06.007

Nogueira V, Lopes I, Freitas AC, Rocha-Santos TAP, Gonçalves F, Duarte AC, et al (2015) Biological treatment with fungi of olive mill wastewater pre-treated by photocatalytic oxidation with nanomaterials. Ecotoxicol Environ Saf [Internet] 115:234–242. Available from: https://doi.org/10.1016/j.ecoenv.2015.02.028

Noorimotlagh Z, Mirzaee SA, Martinez SS, Alavi S, Ahmadi M, Jaafarzadeh N (2019) Adsorption of textile dye in activated carbons prepared from DVD and CD wastes modified with multiwall carbon nanotubes: Equilibrium isotherms, kinetics and thermodynamic study. Chem Eng Res Des [Internet] 141:290–301. Available from: https://doi.org/10.1016/j.cherd.2018.11.007

Nzila A (2018) Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons under anaerobic conditions: overview of studies, proposed pathways and future perspectives. Environ Pollut [Internet] 239:788–802. Available from: https://doi.org/10.1016/j.envpol.2018.04.074

Ochando-Pulido JM, González-Hernández R, Martinez-Ferez A (2018) On the effect of the operating parameters for two-phase olive-oil washing wastewater combined phenolic compounds recovery and reclamation by novel ion exchange resins. Sep Purif Technol [Internet] 195(December 2017):50–59. Available from: https://doi.org/10.1016/j.seppur.2017.11.075

Pérez LS, Rodriguez OM, Reyna S, Sánchez-Salas JL, Lozada JD, Quiroz MA et al (2016) Oil refinery wastewater treatment using coupled electrocoagulation and fixed film biological processes. Phys Chem Earth 91:53–60

Pi Y, Li X, Xia Q, Wu J, Li Y, Xiao J, et al (2018) Adsorptive and photocatalytic removal of Persistent Organic Pollutants (POPs) in water by metal-organic frameworks (MOFs). Chem Eng J [Internet] 337(December 2017):351–371. Available from: https://doi.org/10.1016/j.cej.2017.12.092

Prabakar D, Suvetha K S, Manimudi VT, Mathimani T, Kumar G, Rene ER, et al (2018) Pretreatment technologies for industrial effluents: critical review on bioenergy production and environmental concerns. J Environ Manage [Internet] 218:165–180. Available from: https://doi.org/10.1016/j.jenvman.2018.03.136

Prakash R, Majumder SK, Singh A (2018) Flotation technique: its mechanisms and design parameters. Chem Eng Process Process Intensif 127(March):249–270

Quan X, Shi H, Zhang Y, Wang J, Qian Y (2004) Biodegradation of 2,4-dichlorophenol and phenol in an airlift inner-loop bioreactor immobilized with Achromobacter sp. Sep Purif Technol 34(1–3):97–103

Radwan M, Gar Alalm M, El-Etriby HK (2019) Application of electro-Fenton process for treatment of water contaminated with benzene, toluene, and p-xylene (BTX) using affordable electrodes. J Water Process Eng [Internet] 31(January):100837. Available from: https://doi.org/10.1016/j.jwpe.2019.100837

Rajkumar D, Palanivelu K (2004) Electrochemical treatment of industrial wastewater. J Hazard Mater 113(1–3):123–129

Rana S, Gupta N, Rana RS (2018) Removal of organic pollutant with the use of rotating biological contactor. Mater Today Proc [Internet] 5(2):4218–4224. Available from: https://doi.org/10.1016/j.matpr.2017.11.685

Rasalingam S, Peng R, Koodali RT (2014) Removal of hazardous pollutants from wastewaters: applications of TiO 2 -SiO 2 mixed oxide materials. J Nanomater 2014(January):1–42

Reungoat J, Escher BI, Macova M, Argaud FX, Gernjak W, Keller J (2012) Ozonation and biological activated carbon filtration of wastewater treatment plant effluents. Water Res [Internet] 46(3):863–872. Available from: https://doi.org/10.1016/j.watres.2011.11.064

Ruan B, Wu P, Chen M, Lai X, Chen L, Yu L, et al (2018) Immobilization of Sphingomonas sp. GY2B in polyvinyl alcohol–alginate–kaolin beads for efficient degradation of phenol against unfavorable environmental factors. Ecotoxicol Environ Saf [Internet] 162(June):103–111. Available from: https://doi.org/10.1016/j.ecoenv.2018.06.058

Sadhukhan J, Martinez-Hernandez E, Murphy RJ, Ng DKS, Hassim MH, Siew Ng K et al (2018) Role of bioenergy, biorefinery and bioeconomy in sustainable development: strategic pathways for Malaysia. Renew Sustain Energy Rev 81(April 2017):1966–1987

Sahinkaya E, Uzal N, Yetis U, Dilek FB (2008) Biological treatment and nanofiltration of denim textile wastewater for reuse. J Hazard Mater 153:1142–1148

Samaei SM, Gato-Trinidad S, Altaee A (2018) The application of pressure-driven ceramic membrane technology for the treatment of industrial wastewaters – a review. Sep Purif Technol [Internet] 200(February):198–220. Available from: https://doi.org/10.1016/j.seppur.2018.02.041

Santos CE, Fonseca A, Kumar E, Bhatnagar A, Vilar VJP, Botelho CMS, et al (2015) Performance evaluation of the main units of a re fi nery wastewater treatment plant – a case study. Biochem Pharmacol [Internet] 3(3):2095–2103. Available from: https://doi.org/10.1016/j.jece.2015.07.011

Schaar H, Clara M, Gans O, Kreuzinger N (2010) Micropollutant removal during biological wastewater treatment and a subsequent ozonation step. Environ Pollut [Internet] 158(5):1399–1404. Available from: https://doi.org/10.1016/j.envpol.2009.12.038

Shetty KV, Kalifathulla I, Srinikethan G (2007) Performance of pulsed plate bioreactor for biodegradation of phenol. J Hazard Mater 140(1–2):346–352

Shetty KV, Verma DK, Srinikethan G (2011) Modelling and simulation of steady-state phenol degradation in a pulsed plate bioreactor with immobilised cells of Nocardia hydrocarbonoxydans. Bioprocess Biosyst Eng. 34(1):45–56

Shiying Y, Ping W, Xin Y, Guang W, Wenyi Z, Liang S (2009) A novel advanced oxidation process to degrade organic pollutants in wastewater: microwave-activated persulfate oxidation. J Environ Sci 21:1175–1180

Singh P, Borthakur A (2018) A review on biodegradation and photocatalytic degradation of organic pollutants: a bibliometric and comparative analysis. J Clean Prod [Internet] 196:1669–1680. Available from: https://doi.org/10.1016/j.jclepro.2018.05.289

Sirtori C, Zapata A, Oller I, Gernjak W, Agüera A, Malato S (2009) Decontamination industrial pharmaceutical wastewater by combining solar photo-Fenton and biological treatment. Water Res 43(3):661–668

Sivagami K, Anand D, Divyapriya G, Nambi I (2019) Treatment of petroleum oil spill sludge using the combined ultrasound and Fenton oxidation process. Ultrason Sonochem [Internet] 51(September 2018):340–349. Available from: https://doi.org/10.1016/j.ultsonch.2018.09.007

Sonune A, Ghate R (2004) DESALINATION Developments in wastewater treatment methods. Desalination [Internet] 167(167):55–63. Available from: www.elsevier.com/locate/desal

Srikanth S, Kumar M, Puri SK (2018) Bio-electrochemical system (BES) as an innovative approach for sustainable waste management in petroleum industry. Bioresour Technol [Internet] 265(December 2017):506–518. Available from: https://doi.org/10.1016/j.biortech.2018.02.059

Sun M, Wei Q, Shao Y, Du B, Yan T, Yan L, et al (2018) Engineering composition-tunable 3D hierarchical bismuth oxyiodides heterojunctions: Ionic liquid-assisted fabrication with strong adsorption ability and enhanced photocatalytic properties. Appl Catal B Environ [Internet] 233(March):250–259. Available from: https://doi.org/10.1016/j.apcatb.2018.04.010

Surkatti R, Al-Zuhair S (2018) Effect of cresols treatment by microalgae on the cells' composition. J Water Process Eng [Internet] 26(October):250–256. Available from: https://doi.org/10.1016/j.jwpe.2018.10.022

Surkatti R, El-Naas MH (2014) Biological treatment of wastewater contaminated with p-cresol using Pseudomonas putida immobilized in polyvinyl alcohol (PVA) gel. J Water Process Eng [Internet] 1:84–90. Available from: https://doi.org/10.1016/j.jwpe.2014.03.008

Sutton PM, Mishra PN, Crawford PM (1994) Combining biological and physical processes for complete treatment of oily wastewaters. Int Biodeterior Biodegrad 33(1):3–21

Tekin H, Bilkay O, Ataberk SS, Balta TH, Ceribasi IH, Sanin FD et al (2006) Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater. Semantic Scholar 136:258–265

Turan-Ertas T (2001) Biological and physical-chemical treatment of textile dyeing wastewater for color and COD removal. J Environ 23(3):199–206

Urbaniec K, Mikulčić H, Wang Y, Duić N (2018) System integration is a necessity for sustainable development. J Clean Prod 195:122–132

Vinduja V, Balasubramanian N (2013) Electrocoagulation-integrated hybrid membrane processes for the treatment of tannery wastewater. Environ Sci Pollut Res 20:7441–7449

Wang D, Hu Q Yuan, Li M, Wang C, Ji M (2016) Evaluating the removal of organic fraction of commingled chemical industrial wastewater by activated sludge process augmented with powdered activated carbon. Arab J Chem [Internet] 9:S1951–S1961. Available from: https://doi.org/10.1016/j.arabjc.2015.08.031

Wang Y, O'Connor D, Shen Z, Lo IMC, Tsang DCW, Pehkonen S, et al (2019) Green synthesis of nanoparticles for the remediation of contaminated waters and soils: Constituents, synthesizing methods, and influencing factors. J Clean Prod [Internet] 226:540–549. Available from: https://doi.org/10.1016/j.jclepro.2019.04.128

Yan L, Wang Y, Li J, Ma H, Liu H, Li T et al (2014) Comparative study of different electrochemical methods for petroleum refinery wastewater treatment. Desalination 341(1):87–93

Yavuz Y, Koparal AS, Öğütveren ÜB (2010) Treatment of petroleum refinery wastewater by electrochemical methods. Desalination 258(1–3):201–205

Zhang Z, Zhu Z, Shen B, Liu L (2019) Insights into biochar and hydrochar production and applications: A review. Energy [Internet] 171:581–598. Available from: https://doi.org/10.1016/j.energy.2019.01.035

Zhao G, Zhou L, Li Y, Liu X, Ren X, Liu X (2009) Enhancement of phenol degradation using immobilized microorganisms and organic modified montmorillonite in a two-phase partitioning bioreactor. J Hazard Mater 169(1–3):402–410

Zhao W, Sui Q, Huang X (2018) Removal and fate of polycyclic aromatic hydrocarbons in a hybrid anaerobic–anoxic–oxic process for highly toxic coke wastewater treatment. Sci Total Environ [Internet] 635(1239):716–724. Available from: https://doi.org/10.1016/j.scitotenv.2018.04.162

Realistic Approach for Bioremediation of Heterogeneous Recalcitrant Compounds

11

Aparna Yadu, Monalisa Satapathy, Biju Prava Sahariah,
and J. Anandkumar

Abstract

Rapid industrialization and urbanization over the past few decades has resulted in the massive contamination of the environmental resources such as air, water, and soil. A wide variety of industrial activities and operation such as discharge or dumping of effluents, accidental leakage and spills, and fugitive emission are responsible for contamination of environment. Heterogeneous compounds generated from industries include organic as well as inorganic anthropogenic compounds such as polycyclic aromatic hydrocarbons, alkyl benzenes (benzene, toluene, xylene, and ethyl benzene), volatile organic compounds, persistent organic pollutants, and oxyanions (nitrate, sulfate, chromate, etc.). Nowadays, management of these pollutants in industries with conventional methods is a highly challenging task due to their toxicity, mutagenicity, and carcinogenicity and their being recalcitrant to natural degradation. To overcome the challenges associated with the above heterogeneous compounds, a modified biodegradation method could be adopted for the effective elimination of these toxic recalcitrants and their derivatives from the industrial effluents. This chapter aims to describe the emission of recalcitrant from different industries, challenges, accessible treatment techniques with their merits as well as demerits, and realistic approach for treatment of heterogeneous compounds by modified sequential bioreactor system to achieve zero pollutant emission.

A. Yadu · M. Satapathy · J. Anandkumar (✉)
Department of Chemical Engineering, National Institute of Technology Raipur,
Raipur, Chhattisgarh, India
e-mail: anandj.che@nitrr.ac.in

B. P. Sahariah
Department of Energy and Environmental Engineering, Chhattisgarh Swami Vivekanand
Technical University, Bhilai, Chhattisgarh, India

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_11

Keywords
Biodegradation · Heterogeneous pollutants · Recalcitrant · Industrial effluent treatment · Organic compounds

11.1 Introduction

Water is a tremendously available natural resource on the earth. Owing to huge industrialization and urbanization, water pollution becomes a worldwide problem. According to the United Nations world population prospects 2017 revision, the current world population is 7.6 billion which is expected to be 8.6 billion in 2030 and 98 billion in 2050. Based on the population growth rate, requirement of clean and safe water will be more in the forthcoming years. Sustainable and clean water cycles are utmost priority policy of various countries in the world. Therefore, it is the essential requisite for present environment to protect the water from being polluted or to develop any cost-effective method. An illogical and rapid global human activity reverberates into environmental deterioration (Singh and Singh 2019). In the present scenario, enormous development of various types of industries gives rise to economic capital of country but at the same time led to the production of hazardous compounds which has caused global deterioration of ecosystem. These industries use huge amount of potable water for different kinds of industrial processes and release the wastewater which contains numerous hazardous pollutants which affect the flora and fauna. Nowadays, contamination of surface water, land water, ground water, sediments, and air due to their contact with hazardous and toxic chemicals is a serious issue throughout the world (Barcelo and Kostianoy 2016). Generally, pollution is caused by heterogeneous compounds such as organics (polycyclic aromatic hydrocarbons (PAHs), alkyl benzenes, volatile organic compounds (VOCs), persistent organic pollutants (POPs)), inorganics (oxyanions), nutrients, heavy metals, and several micro pollutants with its derivatives such as pesticides, antibiotics, disinfection by-products (DBPs), endocrine-disrupting compounds (EDCs), personal care products (PCPs), and pharmaceuticals (Bui et al. 2019). All of these pollutants are considered to be the most dangerous due to its intrinsic toxicity, recalcitrant behavior, and high exposure level to the environment. Therefore, these pollutants have been blacklisted and placed on priority list by several environmental protection agencies. However, there is no probability to stop the release of wastewater into the environment. The conventional treatment methods are feasible to reduce the harmful effects of these pollutants. The different physicochemical treatment methods such as chemical precipitation, adsorption, membrane separation process, advanced oxidation process, ozonation, and ion-exchange are available for removal of these toxic pollutants from the environment at full scale (Wang and Chen 2009). However, these treatment techniques have certain limitations depending on the compound to be removed and their efficiency. In that, certain compounds are removed completely by some methods, few compounds are not removed at all, and some are removed partially by these physicochemical treatment methods (Rajasulochana and Preethy

2016). The problems associated with these techniques can be overcome by biodegradation methods. Biodegradation or bioremediation becomes more popular nowadays because they are cost-effective, energy-saving, and eco-friendly for the treatment of wastewater. Bioremediation is a feasible technology for the removal of organic as well as inorganic pollutants by means of microorganism or detoxification of hazardous/toxic chemicals from the environment (Basha et al. 2010; Pandey et al. 2007).

The major goal of bioremediation technology is transformation of organic pollutants into their less toxic metabolites or mineralization into CO_2 and water. This microbiological process reduces the hydrocarbon concentration to permissible levels so that there will be any chance of an unacceptable risk to the environment/human health (Talley 2006). Since the last decades, plentiful research has been carried out in order to eliminate these hazardous contaminants from the environment by using appropriate treatment methods. The newer ones are applied additionally to the existing conventional treatment techniques. These methods essentially include an extra step or process or application in the earlier methods to achieve the complete removal of hazardous pollutants. In the last few years, intense research is carried out to investigate the applicability of such advanced treatment technologies not only to remove only organic and inorganic contaminants but also to remove microorganisms, antibiotic-resistant bacteria, viruses, and protozoa from wastewater. This chapter provides knowledge about recent updates in bioremediation of recalcitrant compounds, conventional methods available to treat these toxic recalcitrant compounds with their merits and demerits, and application of newly made technology in context to complete the removal of recalcitrant compounds from the environment.

11.2 Classification of Heterogeneous Compounds

The constituents of wastewater are generally classified as organic and inorganic. Inorganic compound in contrast to organic compound is a chemical compound lacking C-H bonds. Some inorganic compounds comprise of carbon or hydrogen atoms in their molecular structure that are often only considered as inorganics such as carbon dioxide (CO_2), carbon monoxide (CO), cyanides (CN^-), thiocyanates (SCN^-), carbides (C_2^-), carbonates (CO_3^-), water (H_2O), and hydrochloric acid (HCl). Mostly inorganic compounds consist of metallic constituents, but not all. In fact, the compounds which are inorganic in nature are found in majority in this universe. The major sources of inorganic compounds (metallic and nonmetallic) in the wastewater are derived from industrial activities, by the addition of mineralized water from wells and groundwater, mining activities, by the release of inorganic chemical wastes, from the farms and agricultural lands, transportation, etc. (Speight 2017).

An organic compound is defined as any chemical compounds which entail carbon and hydrogen atoms also termed as hydrocarbon together covalently linked with oxygen and nitrogen in some cases. In general, molecules of organic compounds are associated with living organism. These typically consist of proteins (40–60%), carbohydrates (25–50%), and oils and fats (8–12%). The broad classifications of heterogeneous compounds are described in the following sections.

11.2.1 Types of Organic Compounds

11.2.1.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons or PAHs are recalcitrant organic compounds comprising of two or more fused benzene rings in linear, cluster, or angular arrangements. Incomplete combustion at high temperature (500–800 °C) or involvement of organic molecules at low temperature (100–300 °C) results in the formation of PAH compounds. PAH in aquatic system comes from accidental leakage, oil spills, atmospheric deposition on sediments, and release of contaminated sediments. PAH generally occurs in oil, coal, and tar deposits. With the increase in molecular weight, their concentration decreases in water owing to their very less hydrophilic property, although they are still the most problematic substances as they pose toxicity threat on ecosystem due to their carcinogenic, teratogenic, and mutagenic nature (Haritash and Kaushik 2009).

11.2.1.2 Alkyl Benzenes

Alkyl benzene or monocyclic aromatics with saturated side chains constitute important class of hydrocarbons. The alkyl benzenes are derivative of benzene in that more than one hydrogen atoms are replaced by alkyl groups of various structures. They are considered as substitute of aromatic hydrocarbons (Francis 1948). The term BTX refers to the mixture of benzene, toluene, and three xylene isomers (ortho, meta, and para) and together comes under the category of aromatic hydrocarbons from the effluent of petroleum refining and petrochemical industries. If ethyl benzene is included in the mixture, the referred mixture is known as BTEX. Benzene, toluene, xylene, and ethyl benzene can be made by several processes. Nevertheless, huge amount of BTEX is produced from the recovery of aromatics during the catalytic reforming of naphtha in petroleum refinery industries. Also, formation of cracked naphtha by steam cracking of hydrocarbons is also responsible for the production of BTX compounds.

11.2.1.3 Volatile Organic Compounds (VOCs)

Volatile organic compound or VOC is any organic chemical compound that has a very high vapor pressure (> 1 mm Hg) at ordinary room temperature (25 °C). The high vapor pressure is due to its low boiling point which causes molecules to evaporate or sublimate at bulk. VOC is categorized in three different ways:

- Very volatile organic compounds (VVOCs)
- Volatile organic compounds (VOCs)
- Semi-volatile organic compounds (SVOCs)

More volatility of compounds is directly related to the higher degree of emission from the surface. Very volatile organic compounds are highly volatile in nature, hence it is difficult to measure, and are found mostly as gases in the air rather than in any kind of materials or on the surfaces. Propane, butane, and methyl chloride are examples of VVOCs (boiling point 50–100 °C), whereas formaldehyde, acetone, ethanol, and hexanol whose boiling point ranges from 50–100 to 240–260 °C are known as VOCs. SVOC boiling point ranges from 240–260 to 380–400 °C, and examples are pesticides, plasticizers, polychlorinated biphenyls (PCB), etc. (USEPA regulations 2019). Volatile organic compounds are of great environmental concern because being in a vapor state, it is very mobile and easily incorporated into the environment. In addition to that, the release of these compounds into public area like treatment plant causes severe effects to plant workers.

11.2.1.4 Persistent Organic Pollutants (POPs)

Persistent organic pollutants (POPs) are of global environmental concern owing to their persistence to environmental degradation, potential for long-term transport, accumulation in the food chain, as well as toxic adverse effects on human health and environment. In general, human being comes in contact with these hazardous compounds in several ways such as food, breathing of air, outdoors, and indoor workplace. POPs are contained in our usable products for daily living (flame retardants, surfactants) which are generally added in order to enhance the product quality. So, it can be said that POPs are available everywhere in this earth in considerable amount. The very much known examples of POPs are pesticides such as DDT, polychlorinated biphenyls (PCB), dioxins, and dibenzofuran. Human exposure to these compounds causes risk of cancer, reproductive disorders, disruption of immune systems, etc. (WHO database 2019; Morabet 2018).

11.2.2 Types of Inorganic Compounds

11.2.2.1 Nitrate

Nitrate, the most highly oxidized form of nitrogen, is an inorganic substance which is formed naturally when nitrogen combines with oxygen or ozone. Nitrogen is essential for the growth of microorganisms, plants, and animals because it works as nutrient or stimulator for them. It is a common contaminant of drinking water and creates serious health problems if present in excessively high concentrations (Seferlis 2008). Nitrate is commonly present in the surface and ground water because it is an end product during aerobic decomposition of organic nitrogenous matter. Significant sources of nitrates include fertilizers, animal feedlots, septic systems, industrial waste, food waste, and drainage from livestock feedlots.

11.2.2.2 Sulfates

In natural environment, sulfur is present in the form of pyrite (FeS_2) and gypsum in sediment ($CaSO_4$), whereas sulfates occur naturally in several minerals includes barite ($BaSO_4$) and epsomite ($MgSO_4.7H_2O$). Point sources of sulfates are sewage treatment plant and municipal or industrial discharge such as tanneries, pulp mills, and textile mills, runoff from fertilized agricultural lands, production of pharmaceutical products, fermentation process, and mining process. Sulfates are generally used in the production of fertilizers, dyes, soaps, shampoos, insecticides, fungicides, sedimentation agents, and plating industries (Klok et al. 2013; Jarvis and Younger 2000). Their solubility in water depends on covalent bonds with specific element like magnesium, potassium and sodium sulfates are more soluble, whereas barium and calcium sulfates and some heavy metals are sparingly soluble in water. Similar to carbon, nitrogen, and phosphorus cycle, a new platform of sulfur-based technologies incorporated with sulfur cycle was developed for the simultaneous removal of possible contaminants like sulfate, carbon, phosphorus, metals, and nitrogen from wastewater (Hao et al. 2014).

11.2.2.3 Heavy Metals

Heavy metals are naturally occurring substances which possess high atomic weight and density relatively more than water. By taking into consideration or assumptions that heaviness and toxicity are correlated, it also includes metalloids such as arsenic which is very toxic at low level of exposure. Environmental contamination by heavy metals nowadays becomes an ecological and global public health concern. Their multiple applications in various places such as industrial, agricultural, domestic, and technological application are responsible for the huge distribution in the environment. The effluent from mining regions generally contains lead, arsenic, copper, chromium, cadmium, and zinc. The release of these heavy metals into the environment leads to contamination of soil, water, and agricultural land (accumulation of metals on food crops and plants) (Verma and Kaur 2016). Among all the above-mentioned heavy metals, chromate is considered as one of the human carcinogen via inhalation. It has high environmental mobility, and it can develop from anthropogenic and natural sources. The major sources of chromium and its derivatives come from chemical industries, dye production, preservation of wood, leather tanning, manufacturing of various alloys, and chrome plating (Zhitkovich 2011).

11.3 Effluents from Various Industries

Tremendously, the main important sources of the pollution of environment are industrial effluent or discharge. A huge amount of wastewater is dumped into the rivers, coastal areas, lakes, and nearby water bodies. Based on different industries and contaminant, there are various types of industrial wastewater; each sector produces its own specific combination of pollutants (Walakira and Okat-okumu 2011). In general industries discharge two types of wastewater such as organic and inorganic industrial wastewater.

11.3.1 Inorganic Wastewater

The main source of industrial inorganic wastewater is coal and steel industry, electroplating plants, iron picking works, commercial enterprises, and nonmetallic industries. This wastewater comprises huge amount of heavy metals, suspended matter, less COD, slag, etc. Mainly inorganic wastewater is produced by the following industries:

- Electric power plants
- Battery manufacturing plant
- Iron and steel industry
- Mines and quarries
- Textile and leather industries
- Microelectronic plant

11.3.2 Organic Industrial Wastewater

Organic industrial wastewater chiefly entails organic waste from those chemical industries which use organic substances for incorporating chemical reactions. The organic wastewater can be removed by means of biological treatment. The industries producing organic wastewaters are as follows:

- Pharmaceuticals, organic dye-stuffs
- Pesticides and herbicides, glue and adhesives, textiles
- Tanneries and leather industries
- Pulp and paper and cellulose manufacturing plants
- Oil refining industries
- Petrochemical industries
- Food and dairy industries
- Brewery and fermentation factories
- Iron and steel industry

11.4 Toxic Effects of Heterogeneous Pollutants

In this section, the different types of organic and inorganic pollutants coming from various industries as well as their toxic effects are demonstrated. The receiving water bodies are polluted by the effluent discharged from industries rendering them

Table 11.1 Toxic effects of heterogeneous pollutants of industrial wastewater

Types of pollutants	Toxic effects
Polycyclic aromatic hydrocarbon (PAH)	PAH compounds are challenging pollutants in terms of removal as it is persistent in the environment due to its low solubility in nature. It affects the living organism due to their acute toxicity, carcinogenicity, and mutagenicity
Alkyl benzenes	They are toxic for living organism as it imparts unpleasant odor
	It adversely affects plant growth and reproductive capacity of the aquatic organism
Volatile organic compounds (VOC)	Short-term exposure: Headache, memory problem, visual disorders, dizziness, eye and skin irritation
	Long-term exposure: Damage of liver, kidney and central nervous system, cancer
Persistent organic pollutants (POP)	The discharge of POP-containing wastewater can pose serious health problems. It is considered highly poisonous and has acute toxicity on the living beings. Due to this the liver and respiratory and nervous systems can be damaged.
Inorganic dissolved salts	It stimulates the total dissolved solids concentration in water which ultimately cause scaling in water supplying pipes and unsuitable for irrigation purpose. They are harmful for aquatic life and toxic for human if above permissible limits
Heavy metals	Buildup of heavy metals cause immense effect on flora and fauna, skin rashes, gastrointestinal problem, fluorosis by fluorides, respiratory problems, etc.

unsuitable for drinking and any other purposes. Table 11.1 shows the adverse effects caused by various kinds of pollutants.

11.5 Physicochemical Treatment Techniques with Merits and Demerits

Generally, conventional wastewater treatment method comprises of a combination of physical and chemical processes for the removal of contaminates. The evolution of physicochemical process came in the late 1950s and at the start of 1960s. During that time for the removal of BOD and suspended solids sedimentation, sand filtration, various types of filters such as press, drum, and cartridge filters, coagulation and flocculation processes were used. In between 1980s and 1990s, absorption using activated carbon was adopted by some researchers for nitrification and BOD removal. In the past two decades, membrane processes such as micro-, ultra- and nanofiltration, reverse osmosis, and advanced oxidation process come into the scenario for possible removal of emerging pollutants in tertiary treatment (Dezotti et al. 2011). Different types of physicochemical treatment methods available for removal of heterogeneous pollutants with their merits and demerits are presented in Table 11.2.

Table 11.2 Merits and demerits of conventional methods used for treatment of polluted wastewater

Process	Merits	Demerits	References
Chemical precipitation	Very simple technology and equipment used in this process, economical and efficient at high loading of pollutants, integrated process, effective technique for removal of metals and fluoride, good for COD removal	Large amount of chemical requirement and consumption such as lime, hydrogen sulfide, regular monitoring of physicochemical properties, addition of extra oxidation step if metals are highly complexed, non-efficient in terms of removal of metal ions at low concentration, requirement of adjunction of unusable chemicals used in the treatment, high amount of sludge production	Duan and Gregory (2003), Fontela et al. (2011), Lefebvre et al. (2010) and Matilainen et al. (2010)
Chemical coagulation	It is an economical treatment process extensively used for removal of turbidity and color	More sludge production, not able to remove trace organics	Henze (2001) and Bratby (2006)
Floatation	Able to remove tiny and low-density particles which will require long settling time, ionic and non-ionic collectors, very useful for primary classification, require low retention time, used as a tertiary treatment of pulp and paper industry	Not cost-effective, large maintenance required, selectivity is dependent on pH, chemical required to control the hydrophobicity among the particles to maintain froth characteristics	Sharma and Sanghi (2012), Soune and Ghate (2004) and Forgacs et al. (2004)
Electrocoagulation	Adsorption and degradation can be achieved at the same time, efficient for removal of soluble and insoluble organics	Evolvement of secondary pollutants, comparatively high cost, less efficient in trace organics removal	Barrera-Diaz et al. (2011)

(continued)

Table 11.2 (continued)

Process	Merits	Demerits	References
Ion exchange	Easy to use with other techniques (integrated process), applicable to various flow regimes, well-established and tested technologies, variety of commercial products are available, ease of regeneration, very rapid and efficient physiochemical process, interesting for recovery of metals	Some economic constraints in terms of resin, maintenance, and regeneration cost, requires more spaces if more volume used, clogging of reactors due to rapid saturation, fouling of beads, rejection of resins	Anjaneyulu et al. (2005) and Baraket (2011)
Adsorption	Well-established tertiary treatment techniques, very simple technique, availability of wide range of commercial and natural adsorbents, very efficient process with rapid kinetics, any kind of pollutants organic or inorganics can be removed by this technique, simple equipment required	Nondestructive process, difficulty in regeneration of adsorbents, expensive disposal of potentially toxic spent adsorbent, desire various types of adsorbents, nonselective methods, elimination of adsorbents	Grover et al. (2011), Nguyen et al. (2012) and Ternes et al. (2002)
Advanced oxidation	Possesses efficiency for degradation of trace organics by generation of free radicals, simple, rapid and efficient process, color and odor are well removed, high throughput, no sludge generation, disinfection	Procurement of chemicals, proper management of oxidant, efficiency directly affects by type of oxidant, short half-life of ozone, pretreatment required for removal of solids, formation of toxic intermediate and by products	Belgiorno et al. (2007), Rojas et al. (2011) and Tuhkanen and Marinosa (2010)
Nanofiltration	Good removal in context of trace organics via electrostatic repulsion	Degree of complexity with separation process, formation of concentrated sludge, fouling	Alturki et al. (2010), Bellona et al. (2004) and Nghiem et al. (2004)

11.6 Bioremediation

According to United States of Environmental Protection Agency (USEPA), bioremediation is spontaneous or managed process which involves living microorganism to degrade or transformation of contaminants into less toxic or nontoxic forms, therefore remedying or eliminating from environmental (EPA 1994). The major goal of bioremediation is to stimulate organism with supplement of essential nutrients that enables them to detoxify or destroy the contaminants. Transformation of organic contaminants through microorganism normally occurs due to organism used pollutants or contaminants for self-growth and reproduction because it works as carbon source or food for them and it provides electrons so that organism can extract to obtain energy. Microorganism gains energy through catalyzing energy-releasing chemical reactions which involves breakdown of chemical bonds and transfer of electrons away from the environment. There are two types of bioremediation:

- In situ bioremediation: It refers to remediation at the point of origin. The advantage of in situ bioremediation is that it prevents the spreading of contaminants during transportation.
- Ex situ bioremediation: It refers to remediation when the contaminated waste has been removed from the treatment place. It helps to control the bioremediation products and making the contaminated area free for use.

11.6.1 Conventional Bioremediation Techniques/Reactors

11.6.1.1 Continuous Stirred-Tank Bioreactors (CSTB)

In the continuous stirred-tank bioreactor, the contents of the vessel no longer vary with time, so that microorganism remains in the bioreactor. The most successful continuous systems are with yeasts and bacteria, in that the desired products are the cells or primary metabolite of the compound. Activated sludge process is the most widely used CSTB process in wastewater treatment. Chemostat is a type of CSTB which is used to culture microorganism and study the basic biochemical properties of microbes. In this reactor, liquid is continuously introduced and taken off from the reactor. The main characteristic of ideal CSTB is that the concentration of microorganism and substrates is uniform everywhere throughout the reactor. It is generally used for anaerobic and aerobic treatment of high concentration of organic and inorganic mixtures (Rittmann and McCarty 2012). The removal of various hydrocarbons from industrial wastewater by using mixed microbial consortium in a CSTB is reported in the literature (Gargouri et al. 2011; Geerdink et al. 1996). The schematic representation of CSTB is shown in Fig. 11.1.

11.6.1.2 Fluidized Bed Bioreactors

In the fluidized bed reactor, attachments of microorganism to the carrier are maintained in suspension by upward flow rate of fluid which needs to be treated. The microorganisms attached to the substance are known as biofilm carriers. These may be granular activated carbon (GAC), sand grains, gravels, diatomaceous earth, or any other solids which are resistant to abrasion. Due to upward velocity of the fluid, carriers are in continuous suspension which depends upon the relative density of the carrier to water. The fluidized bed reactor has the advantage to continuously withdraw products and introduce reactants due to its nature of being fluidized. In

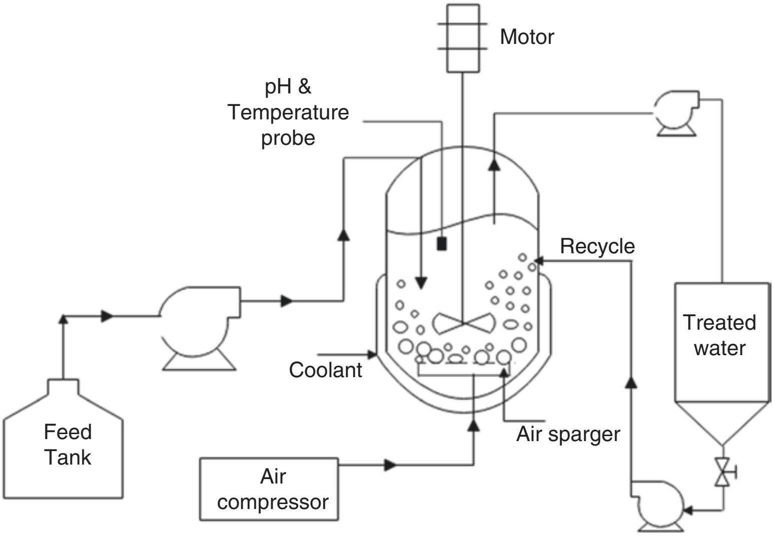


Fig. 11.1 Schematic representation of continuous stirred-tank bioreactor (CSTB)

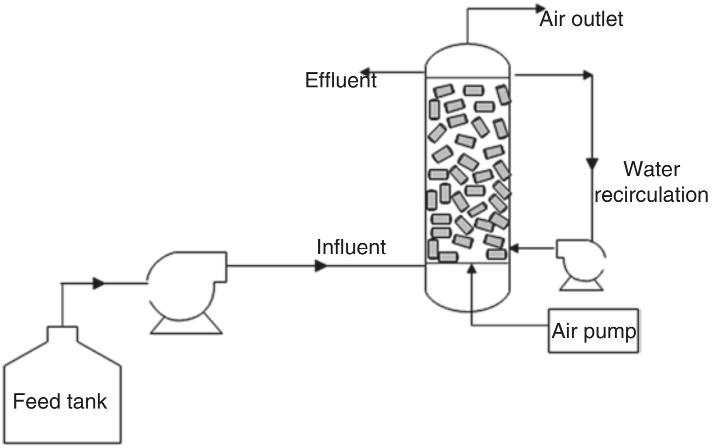


Fig. 11.2 Schematic representation of fluidized bed reactor

continuous process, this reactor allows the manufacturers to produce different products more efficiently rather than batch process. Fluidized bed bioreactors are extensively used for many industrial wastewater treatments such as petroleum wastewater, textile industry effluent, and real acid mine drainage water (Balagi and Poongothai 2012; Banerjee and Ghoshal 2016; Sahinkaya et al. 2011). The basic structure of fluidized bed reactor is shown in Fig. 11.2.

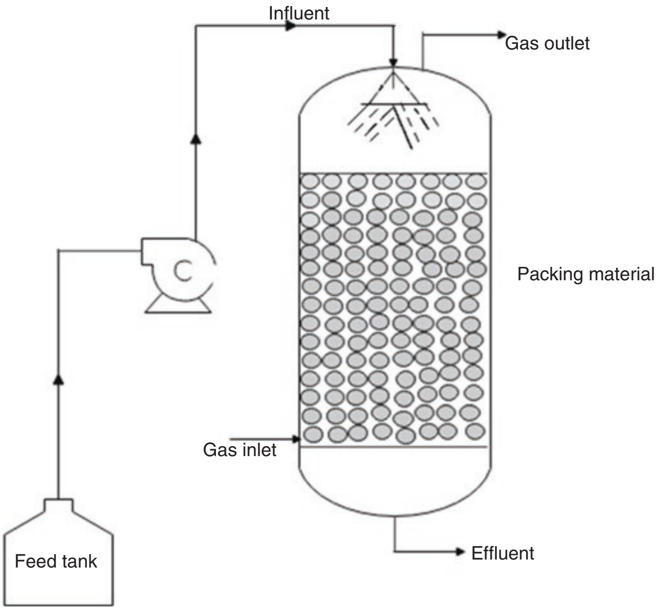


Fig. 11.3 Pictorial representation of packed bed reactor

11.6.1.3 Packed Bed Bioreactor

Generally, packed bed bioreactors are used for aerobic treatment of wastewater in the form of trickling filters. Packed bed reactor is the most common biofilm reactor in which carrier media are stationary. Various kinds of packed bed materials such as rock, slag, plastics, and ceramic can be procured from the commercial market based on the size and requirement according to specific reactors. The arrangement of packing materials in the packed bed reactors can be continuous or in multiple stages. Packed bed reactors can be used for removal of nitrate in denitrification process and also in anaerobic treatment for highly concentrated industrial wastewater. Higher volumetric loading is possible in packed bed reactor. Biodegradation of chlorophenol and fluorine polycyclic aromatic hydrocarbon in packed bed bioreactor system has been reported in the literature by using mixed bacterial consortium and LDPE immobilized *Pseudomonas pseudoalcaligenes*, respectively (Zilouei et al. 2006; Sonwani et al. 2019). Pictorial representation of packed bed reactor is given in Fig. 11.3.

11.6.1.4 Membrane Bioreactor

Membrane bioreactors are basically developed after the ultrafiltration, nanofiltration, microfiltration, and reverse osmosis. In membrane bioreactor, the soluble enzyme and substrate are introduced on one side of the membrane, and from the other side, the product is forced out through the membrane (Fig. 11.4). It is operated with microorganism agglomerated in the form of flocs and preserved in suspension by stirring. The membrane acts as a selective barrier to these flocs. This bioreactor

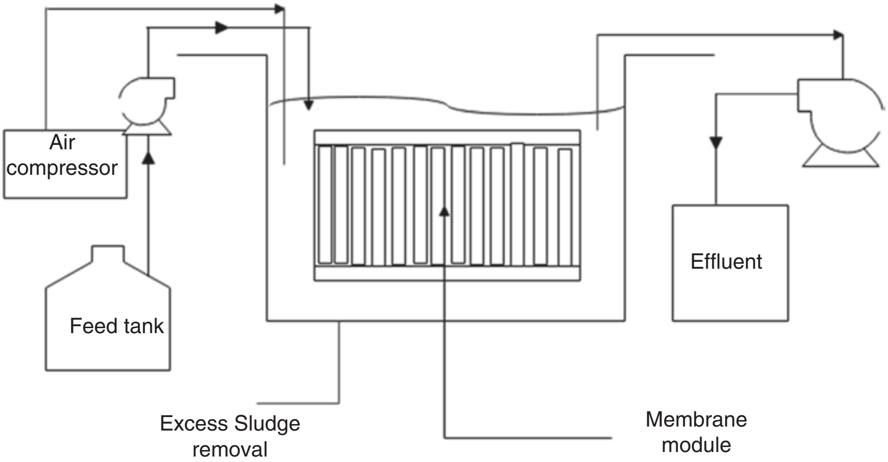


Fig. 11.4 Schematic diagram of membrane bioreactor

permits the separation of flocs (sludge) from the aqueous phase to relative phase. Recently developed submerged membrane bioreactor shows the reduction of energy consumption. In this, hollow fiber membrane module is submerged in the bioreactor system operated in different environmental conditions, i.e., anaerobic, anoxic, and aerobic. Ammonia and phenol up to 1000 mg/L can be removed by using aerobic submerged membrane bioreactor as reported by (Rezakazemi et al. 2018).

11.7 Factors Affecting Biodegradation

11.7.1 Temperature

Temperature is one of the important environmental factors, which can alter the biodegradation ability of the microbes. Different types of microbes can survive in wide range of temperature. The temperature can alter the kinetics. Hence the optimization of temperature is quite essential for conducting biodegradation process. The temperature dependency of reaction rate constant can be estimated by Van't Hoff-Arrhenius relationship (Metcalf and Eddy 2014). The increasing in the temp increases the rate of biodegradation. Most of the fungus and algae are well grow in lower temperature. PAH compounds can be easily biodegraded at high thermophilic range (55 °C). Manzano et al. (1999) have reported about the biodegradation of nonylphenolpolyethoxylate where the growth rate increases with increase in temperature (i.e., 8.936 at 25 °C). Bacterial growth rate is double for each 10 °C hike. At higher temperature the degradation of aromatic compound was more due to the higher metabolic activity and higher bacterial density. Bauer and Capone (1985) reported that the temperature and oxygen content are two important rate-limiting factors for mineralization of PAH compounds. Armenante et al. (1999) discussed about the effect of temperature on the degradation of halogenated phenolic compounds. The rate of dehalogenation increased with increasing in temperature from 25 to 30 °C. The high phenol degradation has been reported by using *P. putida* at 30°C. Here, the rate of degradation increases with increase in temperature (El-Naas et al. 2009).

11.7.2 pH

pH plays a vital role for biodegradation as well as biodeterioration. Lower pH is excellent for the microbial attack. The pH range for the biological growth is 6.5–7.8. The pH of the medium gradually drops down when the growth of the microbes is good. The higher pH inhibits the algal growth (Falkiewicz-Dulik et al. 2015). From the earlier reported literature, PAH compound (phenanthrene) easily degraded at acidic pH (6.5) using *M. vanbaalenii* PYR-1 (Kim et al. 2005). Similarly, Dursun and Tepe (2005) reported that phenol removal and microbial (*Ralstonia eutropha*) growth rate is high at pH 7, but it decreases at acidic and alkaline pH.

11.7.3 C/N Ratio

Microbes require nutrient for their cell growth and replication. If the carbon source is more or less, it affects the overall growth of microbes. Carbon source is an important factor for nitrification/denitrification reaction. The nitrification efficiency and dynamic behavior of nitrifiers and heterotrophs are greatly affected by C/N ratio (Wang et al. 2009). At high C/N ratio, the growth rate of the heterotrophs is more than the nitrifiers (Xia et al. 2008). Hence, the nitrification process is getting retarded in the biodegradation process.

11.7.4 F/M Ratio

Food/microbes ratio is one of the important factors to investigate about the efficacy of the wastewater treatment system. F/M ratio can be adjusted by changing recirculation ratio. Lesser F/M ratio prevents induction of enzymes, and higher F/M ratio is toxic for the microbes, hence increasing the lag phase. The food is considered as COD and BOD loading to the treatment system and microbes present in the existing system. F/M ratio of 0.75 is adequate for biodegradation of phenol in anaerobic condition (Hussain et al. 2009). F/M ratio can also affect the sludge granule size which is important for the aerobic process. High F/M ratio makes faster and bigger size granules (Li et al. 2011).

11.8 Types of Bioprocess

11.8.1 Suspended Growth Process

In this process the microbes used to treat the wastewater are in the form of suspension and by means of mechanical mixing or aeration. The mixed liquor suspended sludge coming from the reactor to the clarifier contains high amount of active microbes which is subjected to recycle to the reactor as seed sludge. The activated sludge process is an example of the suspended growth process which is generally used for the municipal wastewater treatment process. In the suspended growth process, maximum percentage of solids can be separated by gravity settling. In aerobic system the heterotrophic bacteria produce polymeric material in the form of flocks which is continuously circulated through the reactor and comes in contact with the oxidizing organic pollutant. The main objectives of the activated sludge process are to remove the maximum possible oxidizable material and produce biological flocks. These two important factors should be considered at the time of optimization of aerobic suspended growth process. Multiple pollutants such as phenol, cresol, xylenol, quinoline, indole, and cyanide coming in coke oven wastewater are efficiently treated using aerobic suspended growth process (Sharma et al. 2018). Degradation of phenanthrene is also reported using mixed microbial culture under aerobic condition (Yuan et al. 2000).

11.8.2 Attached Growth Process

In this process the microbes are attached to a support medium, and the support medium can be a fixed one or a moving one. The microorganisms degrade the organic material and form a biofilm through which it is attached to the support material. The excess growth of biomass is sloughed from the carrier material and allowed for disposal. Tricking filter, rotating biological contactor, and fluidized bed reactor are the examples of attached growth process. In the past few years, the attached growth process is considered to be the most promising treatment system in the field of environmental engineering. Passive aerated biological filter is one of the emerging treatment systems for the high organic loading wastewater which helps to reduce the energy cost of treatment process (Ismali and Twafik 2016; Abou-Elela et al. 2019). Different types of carrier materials such as jute fiber, plastic fiber, and polyester fiber are effectively used as carrier materials for successfully treating the slaughter house and other wastewaters (Aziz et al. 2018; Rodriguez et al. 2011).

11.9 Modified Bioremediation Techniques for Heterogeneous Compounds

11.9.1 Sequential Bioreactor (SBR) System

Sequential bioreactor system has drawn the attention of many researchers due to its innovative applications in the wastewater treatment. In this treatment more than one reactor is connected series. Sequential bioreactors work on different modes such as filling, mixing, reacting, sedimenting, and decanting. These reactors can be used in various biochemical environments like organic removal followed by nitrification and denitrification. This type of reactors mainly used for removal of toxic organics as well as nitrogen and other inorganic pollutants. Based on the characteristic of the wastewater hydraulic retention time, organic loading rate and sludge retention time can be changed in sequential bioreactor system. Nowadays researchers pay more attention to hybrid treatment systems for wastewater management. Combinations of attached and suspended growth systems are together used in SBR to handle high organic loading (textile industry effluent) and shock loading problems (Shoukat et al. 2019).

11.9.2 Anammox Process

It is also one of the innovative biological treatment processes to treat the ammonia-nitrogen-rich wastewater. In this process, ammonium ion is oxidized into nitrogen gas under anaerobic condition where autotrophic bacteria oxidized and converted inorganic carbon to cellular carbon using nitrite as electron acceptor (Rittmann and McCarty 2012). Anammox process has been used to treat landfill leachate, coke oven wastewater, and pharmaceutical wastewater (Liang et al. 2009; Toh and Ashbolt 2002; Tang et al. 2011). The first full-scale anammox treatment plant was established and operated in the Netherlands (Jin et al. 2012). Anammox bacteria possess slow growth rate and less yield and are very much sensitive to other environment conditions. Hence, it is difficult to grow the anammox bacteria and maintain suitable environment for this process which is the main drawback of this process. Excess amount of ammonium-nitrogen also shows the inhibitory impact to the anammox bacteria. The release of free ammonia from the anammox process leads to reduce the process efficiency. Synergistic effect of anammox bacterial with denitrifying bacteria is also mentioned in literature. But it is difficult to maintain the dissolved oxygen and pH in a single reactor. Therefore to overcome these issues, the pH of this process should be always maintained at neutral condition. Some additional pretreatment techniques must be adopted to treat the inhibitory compounds present along with other pollutants. Anammox sludge should be intermittently added to maintain the good quantity of anammox bacteria within the reactor. Dissolved oxygen is also a key factor for anammox process; therefore air saturation level should be maintained between 2% and 18% (Jin et al. 2012).

11.9.3 SHARON Process

SHARON (single reactor system for high ammonium removal over nitrite) process is used to treat high-nitrogen-comprising wastewater. This process takes place at high temperature (35 °C) using intermittently aerated CSTB with less retention time. Both AOB (ammonia oxidizing bacteria) and NOB (Nitrite oxidizing bacteria) are essential to operate this system. NOB is commonly washed out due to less retention time and therefore nitrite only formed in SHARON reactor that reduces the pH. This process needs only less than 25% of oxygen and 40% of carbon source to convert the nitrite from ammonia than nitrate (Van Dongen et al. 2001). SHARON process coupled with anammox process is used to treat the landfill leachate and refinery wastewater which contain high amount of nitrogen with cyanide, phenol, and sulfide (Shalini and Joseph 2018; Milia et al. 2012). Here, SHARON process used followed by anammox process.

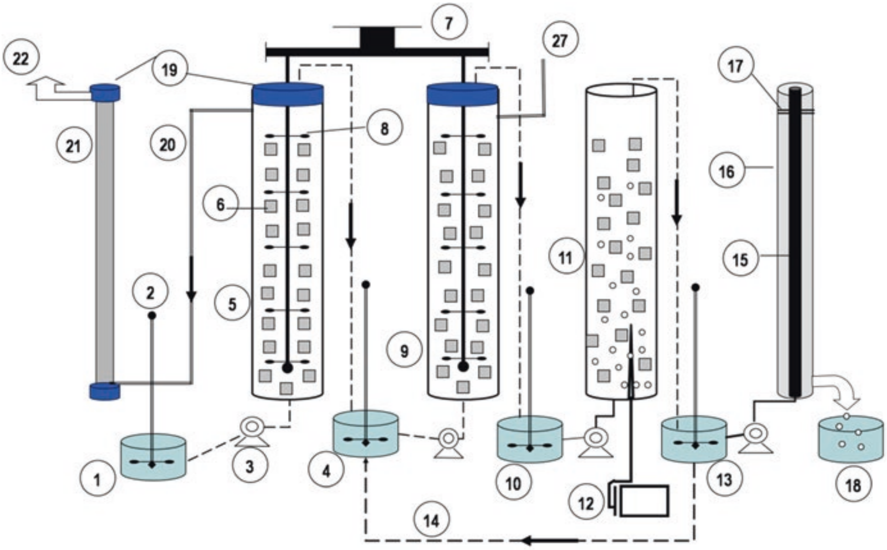
11.9.4 Moving Bed Bioreactor (MBBR)

MBBR technology developed from the activated sludge process and bio filter process. In MBBR different types of carrier material were used over which the biomass can grow. MBBR is connected in series to establish the sequential MBBR to achieve the continuous contact of biomass with pollutants. Selection of biomass carrier material in MBBR is one of the key factors which enhance the growth of biomass with higher surface area (e.g., polyurethane foam, polyethylene media, etc.). MBBR can also be operated in different environments (i.e., anaerobic, aerobic, and anoxic). Biomass in MBBR can be in suspended or attached form. This process has many advantages such as no sludge bulking issues, less sludge production, and resistance to higher organic loading and shows very good removal efficiency. MBBR is successfully used for treatment of slaughter house and refinery wastewater. Coke oven wastewater containing a variety of pollutants and phenolic wastewater can also be efficiently treated by MBBR (Sahariah et al. 2016; Borghai and Hosseini 2004). It can be used as potential treatment technique with high sludge retaining time.

11.9.5 Modern Hybrid Systems

Combination of two or more treatments combined in a single system to achieve the zero pollutant discharge is called as hybrid treatment system. For instance, (a) suspended cum attached growth process and (b) sequential bioreactor combined with physicochemical reactor are some of the familiar hybrid systems. Use of the biological process in real field at higher scale is a big challenge for the environmental engineers due to the persistence nature. Recently researchers have developed many novel hybrid techniques to handle the multi-toxic compounds. In this context three-stage anaerobic-anoxic-aerobic and four-stage anaerobic-anoxic-oxic-oxic bioreactors have been developed and successfully used for treatment of refractory chemical and PAH compounds present in coke oven wastewater (Zhou et al. 2017, 2018). Novel integrated hybrid treatment approach is also an advanced treatment strategy in the field of environmental engineering. Recently, Ren et al. (2019) have reported that integrated hybrid process can be used as efficient technique to treat the PAHs, phenols, BTEXs, and heterocyclic compounds coming from coking wastewater reclamation plant. In this study, anaerobic-aerobic-coagulation-sand filter-ultrafiltration- adsorption-nanofiltration-RO system has been proposed to target each pollutant for efficient removal in a specific unit according to its characteristics.

The addition of gas absorption unit in the hybrid process can be another value addition to the integrated hybrid treatment system. Recently, a potential hybrid system has been developed in the field of biological wastewater treatment which is known as integrated biophysical hybrid reactor system (Anandkumar 2016). It is a combination of sequential physical and biological process. The integrated biophysical hybrid reactor system is established for the remediation of high loading of organic and inorganic pollutants or heterogeneous pollutants resulting from various processes of industries. This hybrid reactor comprises of three units, namely, anaerobic-anoxic-aerobic sequential bioreactor, gas absorption unit, and polishing



1. Feed tank, 2. Stirrer, 3. Peristaltic pump, 4. Anaerobic reactor, 5. Anaerobic effluent, 6. Sponge cube, 7. Mechanical stirrer, 8. Baffle, 9. Anoxic reactor, 10. Anoxic effluent, 11. Aerobic reactor, 12. Aerator, 13. Aerobic effluent, 14. Recycle, 15. Cationic packed bed column, 16. Anionic packed bed column, 17. Connector of cationic and anionic column, 18. Final effluent outlet, 19. Air tight cover, 20. Gas collecting tube, 21. Gas adsorption column and 22. Exit gas tube

Fig. 11.5 Schematic diagram of biophysical hybrid reactor system unit. The integrated biophysical hybrid reactor system is shown in Fig. 11.5. In the first step, a three-stage anaerobic-anoxic-aerobic sequential bioreactor system is used wherein each reactor consists of three equal sections packed with sponge cubes as biomass carrier to obtain the maximum pollutant removal efficiency. Secondly, in gas absorption unit low-cost and recyclable adsorbent is used for the removal of various gaseous by-products coming from the anaerobic and anoxic units. In the third stage, surface-modified coal fly ash-based cationic and anionic ceramic adsorbents are packed in the inbuilt cationic-anionic polishing unit to achieve the zero pollutant discharge in the effluent after treatment.

11.10 Conclusion and Future Scope

This chapter describes the different types of heterogeneous pollutants coming from industrial effluents and their toxic effects. Various physicochemical treatment techniques exist to handle these pollutants, and their merits and demerits are discussed. Also, it comprises different biological treatment processes applied for treatment of pollutants coming from different industries. Different types of bioreactors as well as newly modified processes and the factors affecting the biodegradation process are included. Biological treatment processes have many advantages as well as some limitation. Considering these limitations of bioprocess therefore users can modify the process according to the necessity. Some researchers have recently developed new hybrid bioreactor systems with certain modifications to handle the heterogeneous pollutants to attain the zero pollutant discharge in the effluent which shows the realistic approach of the biological wastewater treatment system. In future, there will be a great demand for eco-friendly hybrid systems in clean technologies to deal the global water pollution challenges.

Acknowledgments The authors would like to thank the Science and Engineering Research Board (DST), Govt. of India, for allowing them to use the project-related information (SB/EMEQ-107/2014) to write this chapter.

References

Abou-Elela SI, Hellal MS, Aly OH, Abo-Elenin SA (2019) Decentralized wastewater treatment using passively aerated biological filter. J Environ Technol 40:250–260

Alturki AA, Tadkaew N, McDonald JA, Khan SJ, Price WE, Nghiem LD (2010) Combining MBR and NF/RO membrane filtration for the removal of trace organics in indirect potable water reuse applications. J Membr Sci 365:206–215

Anandkumar J (2016) Combined novel bio-physical treatment for heterogeneous wastewater pollutants. SERB-DST Sponsored Project, Government of India

Anjaneyulu Y, Sreedhara Chary N, Samuel Suman Raj D (2005) Decolourization of industrial effluents: available methods and emerging technologies—a review. Rev Environ Sci Biotechnol 4:245–273

Armenante PM, Kafkewitz D, Lewandowski GA, Jou CJ (1999) Anaerobic–aerobic treatment of halogenated phenolic compounds. J Water Res 33(3):681–692

Aziz H, Puat N, Alazaiza M, Hung YT (2018) Poultry slaughterhouse wastewater treatment using submerged fibers in an attached growth sequential batch reactor. J Environ Res Public Health 15(8):1734

Balaji K, Poongothai S (2012) Evaluation of fluidized bed reactor in treating dyeing effluent. Int J Eng Sci Technol 4(7):3134–3139

Banerjee A, Ghoshal AK (2016) Biodegradation of real petroleum wastewater by immobilized hyper phenol-tolerant strains of Bacillus cereus in a fluidized bed bioreactor. 3 Biotech 6(2):137

Barakat MA (2011) New trends in removing heavy metals from industrial wastewater. Arab J Chem 4:361–377

Barcelo D, Kostianoy AG (2016) Advanced treatment technologies for urban wastewater reuse. Springer, Cham

Barrera-Dıaz C, Bilyeu B, Roa G, Bernal-Martinez L (2011) Physicochemical aspects of electrocoagulation. Sep Purif Rev 40:1–24

Basha KM, Rajendran A, Thangavelu V (2010) Recent advances in the biodegradation of phenol: a review. Asian J Exp Biol Sci 1:219–234

Bauer JE, Capone DG (1985) Degradation and mineralization of the polycyclic aromatic hydrocarbons anthracene and naphthalene in intertidal marine sediments. J Appl Environ Microbiol 50(1):81–90

Belgiorno V, Rizzo L, Fatta D, Della Rocca C, Lofrano G, Nikolaou A, Naddeo V, Meric S (2007) Review on endocrine disrupting-emerging compounds in urban wastewater: occurrence and removal by photocatalysis and ultrasonic irradiation for wastewater reuse. Desalination 215:166–176

Bellona C, Drewes JE, Xu P, Amy G (2004) Factors affecting the rejection of organic solutes during NF/RO treatment—a literature review. Water Res 38:2795–2809

Borghei SM, Hosseini SH (2004) The treatment of phenolic wastewater using a moving bed biofilm reactor. J Process Biochem 39(10):1177–1181

Bratby J (2006) Coagulation and flocculation in water and wastewater treatment, vol 407. IWA Publishing, London

Bui XT, Chiemchaisri C, Fujioka T, Varjani S (2019) Introduction to recent advances in water and wastewater treatment technologies. In: Energy, environment and sustainability. Springer, Singapore

Dezotti M, Lippel G, Bassin JP (2011) Emerging, consolidated technologies and introduction to molecular techniques. In: Advances biological process for wastewater treatment. Springer, Rio de Janeiro

Duan J, Gregory J (2003) Coagulation by hydrolysing metal salts. Adv Colloid Interf Sci 100–102:475–502

Dursun AY, Tepe O (2005) Internal mass transfer effect on biodegradation of phenol by Ca- alginate immobilized Ralstoniaeutropha. J Hazrad Mater 126(1–3):105–111

El-Naas MH, Al-Muhtaseb SA, Makhlouf S (2009) Biodegradation of phenol by Pseudomonas putida immobilized in polyvinyl alcohol (PVA) gel. J Hazard Mater 164(2–3):720–725

Environmental Protection Agency (EPA) (1994) Assessment and remediation of contaminate sediments (ARCS) program, final summary report, EPA-905-S-94-001. EPA, Chicago

Falkiewicz-Dulik M, Janda K, Wypych G (2015) Handbook of material biodegradation, biodeterioration and biostabilization, 2nd edn. Chem Tech Publishing United States, Toronto

Food Safety WHO (2019). https://www.epa.gov/indoor-air-quality-iaq/technical-overview-volatile-organic-compounds. Accessed 25 May 2019

Forgacs E, Cserhati T, Oros G (2004) Removal of synthetic dyes from wastewaters: a review. Environ Int 30:953–971

Francis AW (1948) Properties of alkylbenzenes. Chem Rev 42(1):107–162

Gargouri B, Karray F, Mhiri N, Aloui F, Sayadi S (2011) Application of a continuously stirred tank bioreactor (CSTR) for bioremediation of hydrocarbon-rich industrial wastewater effluents. J Hazard Mater 189(1–2):427–434

Geerdink MJ, van Loosdrecht MM, Luyben KCA (1996) Biodegradability of diesel oil. Biodegradation 7(1):73–81

Grover DP, Zhou JL, Frickers PE, Readman JW (2011) Improved removal of estrogenic and pharmaceutical compounds in sewage effluent by full scale granular activated carbon: impact on receiving river water. J Hazard Mater 185:1005–1011

Hao Tian-wei, Peng-yu X, Mackey HR, Chi K, Lu H, Ho-kwong C, Loosedrecht MCM van, Guang-Hao C (2014) A review of biological sulfate conversion in wastewater treatment. Water Res 65:1–21

Haritash AK, Kaushik CP (2009) Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review. J Hazard Mater 169:1–15

Henze M (2001) Wastewater treatment—biological and chemical processes. Springer, Berlin

Huerta-Fontela M, Galceran MT, Ventura F (2011) Occurrence and removal of pharmaceuticals and hormones through drinking water treatment. Water Res 45:1432–1442

Hussain A, Parveen T, Kumar P, Mehrotra I (2009) Phenolic wastewater: effect of F/M on anaerobic degradation. Desalin Water Treat 2(1–3):260–265

Ismail S, Tawfik A (2016) Performance of passive aerated immobilized biomass reactor coupled with Fenton process for treatment of landfill leachate. Int Biodeterior Biodegradation 111:22–30

Jarvis AP, Younger PL (2000) Broadening the scope of mine water environmental impact assessment: a UK perspective. Environ Impact Assess 20:85–96

Jin RC, Yang GF, Yu JJ, Zheng P (2012) The inhibition of the Anammox process: a review. J Chem Eng 197:67–79

Kim YH, Freeman JP, Moody JD, Engesser KH, Cerniglia CE (2005) Effects of pH on the degradation of phenanthrene and pyrene by Mycobacterium vanbaalenii PYR-1. J Appl Microbial Biotechnol 67(2):275–285

Klok JBM, de Graff M, van den Bosch PLF, Bolee NC, Keesman KJ, Janssen AJH (2013) A physiologically based kinetic model for bacterial sulfide oxidation. Water Res 47:483–492

Lefebvre O, Lee LY, Ng HY (2010) Physicochemical treatment of micropollutants: coagulation and membrane processes. In: Virkutyte J, Jegatheesan V, Varma RS (eds) Treatments of micropollutants in water and wastewater. IWA Publishing, London, pp 205–237

Li AJ, Li XY, Yu HQ (2011) Effect of the food-to-microorganism (F/M) ratio on the formation and size of aerobic sludge granules. Process Biochem 46(12):2269–2276

Liang Z, Liu JX, Li J (2009) Decomposition and mineralization of aquatic humic substances (AHS) in treating landfill leachate using the Anammox process. Chemosphere 74(10):1315–1320

Manzano MA, Perales JA, Sales D, Quiroga JM (1999) The effect of temperature on the biodegradation of a nonylphenolpolyethoxylate in river water. Water Res 33(11):2593–2600

Matilainen A, Vepsalainen M, Sillanpaa M (2010) Natural organic matter removal by coagulation during drinking water treatment: a review. Adv Colloid Interf Sci 159:189–197

Metcalf & Eddy (2014) Wastewater engineering: treatment and reuse, 5th edn. Mc-Graw Hill Publication, New York

Milia S, Cappai G, Perra M, Carucci A (2012) Biological treatment of nitrogen-rich refinery wastewater by partial nitritation (SHARON) process. Environ Technol 33(13):1477–1483

Morabet RE (2018) Effect of outdoor air pollution on human health. In: Reference module in earth systems and environmental sciences. Elsevier, Amsterdam

Nghiem LD, Manis A, Soldenhoff K, Schafer AI (2004) Estrogenic hormone removal from wastewater using NF/RO membranes. J Membr Sci 242:37–45

Nguyen LN, Hai FI, Kang J, Price WE, Nghiem LD (2012) Removal of trace organic contaminants by a membrane bioreactor—granular activated carbon (MBR–GAC) system. Bioresour Technol 113:169–173

Pandey A, Singh P, Iyenger L (2007) Bacterial decolorization and degradation of azo dyes. Int Biodeterior Biodegradation 59:73–84

Rajasulochana P, Preethy V (2016) Comparison on efficiency of various techniques in treatment of waste and sewage water-a comprehensive review. Resour Eff Technol 2:175–184

Ren J, Li J, Li J, Chen Z, Cheng F (2019) Tracking multiple aromatic compounds in a full-scale coking wastewater reclamation plant: interaction with biological and advanced treatments. Chemosphere 222:431–439

Rezakazemi M, Maghami M, Mohammadi T (2018) Wastewaters treatment containing phenol and ammonium using aerobic submerged membrane bioreactor. Chem Cent J 12(1):79

Rittmann BE, McCarty PL (2012) Environmental biotechnology: principles and applications. Tata McGraw-Hill Education, New York

Rodríguez DC, Ramirez O, Mesa GP (2011) Behaviour of nitrifying and denitrifying bacteria in a sequencing batch reactor for the removal of ammoniacal nitrogen and organic matter. Desalination 273:447–452

Rojas MR, Leung C, Whitley D, Zhu Y, Arnold RG, Saez AE (2011) Advanced oxidation of trace organics in water by hydrogen peroxide solar photolysis. Ind Eng Chem Res 50:12479–12487

Saferlis P (2008) Measurement and process control for water and energy use in the food industry. In: Handbook of water and energy management in food processing. Elsevier, Burlington

Sahariah BP, Anandkumar J, Chakraborty S (2016) Treatment of coke oven wastewater in an anaerobic–anoxic–aerobic moving bed bioreactor system. J Desalin Water Treat 57(31):14396–14402

Sahinkaya E, Gunes FM, Ucar D, Kaksonen AH (2011) Sulfidogenic fluidized bed treatment of real acid mine drainage water. Bioresour Technol 102(2):683–689

Shalini SS, Joseph K (2018) Combined SHARON and ANAMMOX processes for ammoniacal nitrogen stabilisation in landfill bioreactors. J Bioresour Technol 250:723–732

Sharma SK, Sanghi R (2012) Advances in water treatment and pollution prevention. Springer, Dordrecht

Sharma NK, Philip L, Murty BS (2018) Aerobic degradation of complex organic compounds and cyanides in coke oven wastewater in presence of glucose. In: Sharma AK, Singh VP, Bhattacharjya AK, Kartha SA (eds) Urban ecology, water quality and climate change. Water science and technology library, vol 84. Springer, Cham, pp 293–304

Shoukat R, Khan SJ, Jamal Y (2019) Hybrid anaerobic-aerobic biological treatment for real textile wastewater. J Water Process Eng 29:100804

Singh RL, Singh RP (2019) Advances in biological treatment of industrial waste water and their recycling for a sustainable future. Springer, Singapore

Sonune A, Ghate R (2004) Developments in wastewater treatment methods. Desalination 167:55–63

Sonwani RK, Giri BS, Das T, Singh RS, Rai BN (2019) Biodegradation of fluorine by neoteric LDPE immobilized Pseudomonas pseudoalcaligenes NRSS3 in a packed bed bioreactor and analysis of external mass transfer correlation. Process Biochem 77:106–112

Speight JG (2017) Sources and types of inorganic pollutants. In: Environmental inorganic chemistry for engineers. Elsevier, Cambridge

Talley JW (2006) Bioremediation of recalcitrant compounds. Taylor & Francis, Boca Raton

Tang CJ, Zheng P, Chen TT, Zhang JQ, Mahmood Q, Ding S, Wu DT (2011) Enhanced nitrogen removal from pharmaceutical wastewater using SBA-ANAMMOX process. Water Res 45(1):201–210

Technical overview of volatile organic compounds USEPA (2019). https://www.epa.gov/indoor-air-quality-iaq/technical-overview-volatile-organic-compounds. Accessed 25 May 2019

Ternes TA, Meisenheimer M et al (2002) Removal of pharmaceuticals during drinking water treatment. Environ Sci Technol 36:3855–3863

Toh S, Ashbolt N (2002) Adaptation of anaerobic ammonium-oxidising consortium to synthetic coke-ovens wastewater. Appl Microbiol Biotechnol 59(2–3):344–352

Tuhkanen TA, Marinosa PC (2010) UV irradiation for micropollutant removal from aqueous solutions in the presence of H_2O_2. In: Virkutyte J, Jegatheesan V, Varma RS (eds) Treatments of micropollutants in water and wastewater. IWA Publishing, London, pp 295–316

Van Dongen LGJM, Jetten MSM, van Loosdrecht MC (2001) The combined SHARON/Anammox process. IWA Publishing, London

Verma N, Kaur G (2016) Trends on biosensing systems for heavy metals detection. Compr Anal Chem 74:33–71

Walakira P, Okot-Okumu J (2011) Impact of industrial effluents on water quality of streams in Nakawa-Ntinda, Uganda. Appl Sci Environ Manage 15(2):289–296

Wang J, Chen C (2009) Biosorbents for heavy metals removal and their future. Biotechnol Adv 27:195–226

Wang LK, Pereira NC, Hung Y (2009) Handbook of environmental engineering. Humana Press, Totowa

Xia S, Li J, Wang R (2008) Nitrogen removal performance and microbial community structure dynamics response to carbon nitrogen ratio in a compact suspended carrier biofilm reactor. Ecol Eng 32:256–262

Yuan SY, Wei SH, Chang BV (2000) Biodegradation of polycyclic aromatic hydrocarbons by a mixed culture. Chemosphere 41(9):1463–1468

Zhao W, Sui Q, Huang X (2018) Removal and fate of polycyclic aromatic hydrocarbons in a hybrid anaerobic–anoxic–oxic process for highly toxic coke wastewater treatment. Sci Total Environ 635:716–724

Zhitkovich A (2011) Chromium in drinking water: sources, metabolism and cancer risk. Chem Res Toxicol 24(10):1617–1629

Zhou X, Zhang Z, Li Y (2017) Four-stage biofilm anaerobic–anoxic–oxic–oxic system for strengthening the biological treatment of coking wastewater: COD removal behaviors and biokinetic modeling. RSC Adv 7(38):23714–23726

Zilouei H, Guieysse B, Mattiasson B (2006) Biological degradation of chlorophenols in packed-bed bioreactors using mixed bacterial consortia. Process Biochem 41(5):1083–1089

Bioremediation of Lignin-Rich Pulp and Paper Industry Effluent

12

Swati Baghel, Biju Prava Sahariah, and J. Anandkumar

Abstract

Pulp and paper industry effluent is constantly associated with degraded and dissolved lignin (≈90%) which creates a serious pollution and toxic effects due to its less biodegradability and high concentration of colour. Hence, lignin in pulp and paper mill effluent is essentially treated prior to its final discharge into the environment. Many physicochemical treatment methods such as electrocoagulation, incineration, ozonation and ultrafiltration are available to handle the lignin waste in black liquor. However, usage of these methods is limited in small- and medium-scale industries due to large minerals, acids and energy consumption which make the technology unsatisfactory. Therefore, there is a need for more practical and economically viable method for treatment of lignin in black liquor especially for small-scale industries. Microbial treatment can be a more suitable and viable technique. In microbial treatment, a wide variety of microbes such as fungi, algae and bacteria have been implicated for lignin biodegradation and decolourization of pulping effluent. Hence, lignin biodegradation by potential indigenous ligninolytic strains could be more suitable due to their biochemical versatility and immense environmental adaptability. This chapter describes introduction to pulp and paper industry effluent, different existing treatment methods and issues and biodegradation of lignin-rich effluent by indigenous ligninolytic microbes.

S. Baghel · J. Anandkumar (✉)
Department of Chemical Engineering, National Institute of Technology Raipur, Raipur, Chhattisgarh, India
e-mail: anandj.che@nitrr.ac.in

B. P. Sahariah
Department of Energy and Environmental Engineering, Chhattisgarh Swami Vivekanand Technical University, Bhilai, Chhattisgarh, India

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_12

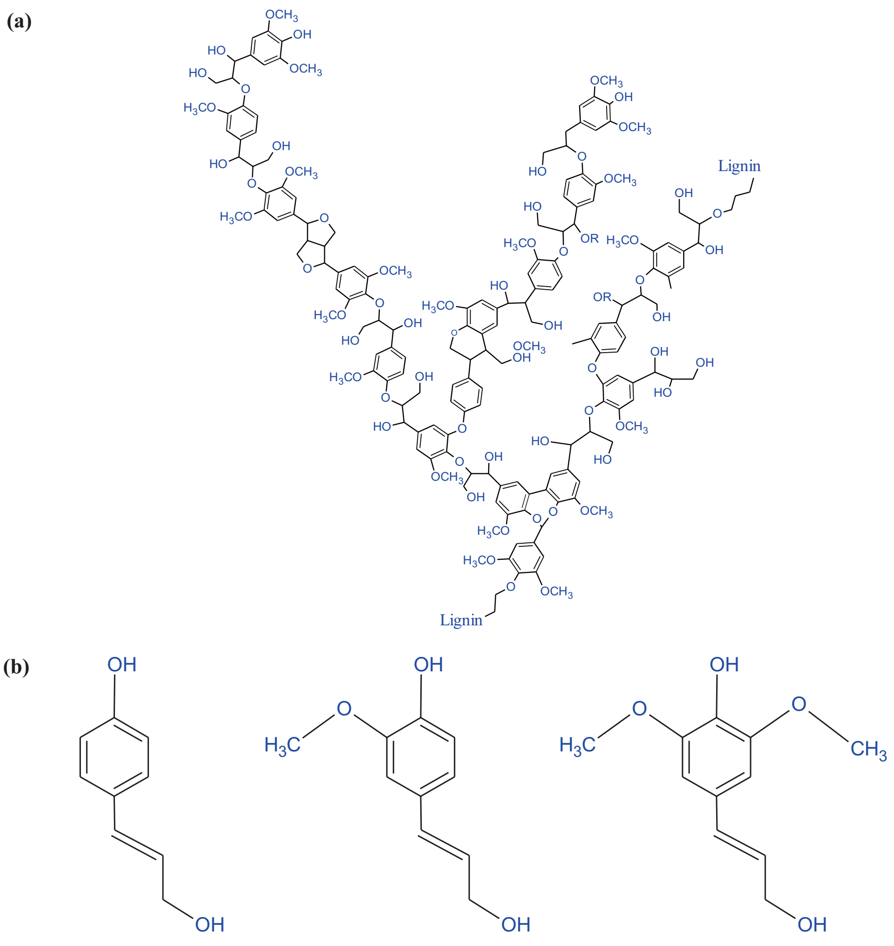
Keywords
Bioremediation · Black liquor · Lignin degradation · Ligninolytic microbes · Pulp and paper mill effluent

12.1 Introduction

Waste management in pulp and paper industries is a challenging task due to its complex and high pollutant load in the effluent. Pulp and paper industries are consuming many resources such as wood (hard wood, soft wood, bamboo and mixed hardwood), non-renewable fossil fuels, electricity, water, non-wood materials and more quantity of chemicals. Approximately 250–300 m^3 water is being used to produce one ton of paper which discharges a mixed variety of gaseous, liquid and solid wastes into the surrounding environment. Industries generally use three types of raw materials such as wood, agricultural residue and recycle waste paper for producing papers. As per the information of Central Pollution Control Board (CPCB), approximately there are 759 unit paper and pulp industries in India. Among this, roughly 30 large-scale units are directly using wood as raw material. Agricultural residues (bagasse, wheat straws, rice straws and cotton stalks) are used in 150 medium-scale industries and the rest of the medium- as well as small-scale industries are using utilized waste paper (domestic released and imported waste paper) as a source for paper manufacturing (Rajwar et al. 2017). There are two major steps followed during paper manufacturing process such as pulping and bleaching. Pulping is a chemical process in which wood chips are treated with alkaline solution of sodium sulfate/sulfite and sodium hydroxide to convert wood chips into pulp at high temperature and pressure. There are three major sources such as cellulose, hemicellulose and lignin are released as by-product during pulping process.

The term 'lignin' is used to explain the complicated organic complex phenolic biopolymers that are binded with cellulose and hemicelluloses to provide the support and forms cell wall structure plants (Bruijnincx et al. 2015). Lignin is a high molecular weight (100 kDa) organic complex compound. Lignin is mainly made by monolignols unites. These monolignols are oxidative polymers of three types of hydroxycinnamyl alcohol sub units such as p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) phenyl propanoid with different structures are shown in Fig.12.1 (Dos et al. 2007 and Higuchi 1990). Every year, approximately 50 million tons of lignin are produced worldwide and released as huge by-products from the pulp and paper industry.

Pulp and paper mill effluent contains a huge amount of lignin which is separated from cellulose and hemicelluloses in pulping during washing process and released as a waste in the effluent. This washed liquid become highly turbid and black in colour due to high concentration of lignin which is called as black liquor (Chaudhry and Paliwal 2018). Moreover, this effluent has high chemical oxygen demand (COD), biochemical oxygen demand (BOD) and chlorinated chemicals (Savant et al. 2006).



4- hydroxyphenyl (H) **Guaiacyl (G)** **Syringyl (S)**

Fig. 12.1 (**a**) Complex structure of lignin and (**b**) types of lignin with different structures

Lignin is much more valuable than just considering as waste. Many useful aromatic monomers are present in the complex lignin structure, and these are released just as a waste without proper treatments in the effluent. The untreated lignin present in the pulp and paper mill effluent creates huge problems during treatment in the effluent treatment plant. So many physicochemical treatment methods such as electrocoagulation, incineration, ozonation and ultrafiltration are available to handle this lignin wastes present in the black liquor. However, these chemical and physicochemical methods have low yield and also consume high energy. Bioremediation is an innovative technology chosen for the cleanup of contaminated sites of industries. Bioremediation of lignin is a natural and also eco-friendly method which plays an important role in producing useful products even after lignin bioremediation with many naturally available microbes such algae, bacteria and fungi (Rahmanpour and Bugg 2015; Su et al. 2018; Moreira et al. 2005; Bugg et al. 2011). Therefore, this chapter is aimed to describe the entire stepwise processes of pulp and paper making industry, various physicochemical treatment techniques available to treat the pulp and paper mill effluent with their merits and demerits as well as the detail discussion on bioremediation of lignin waste present in effluents.

12.2 Processes of Pulp and Paper Making

There are many processes involved in the paper making industries which are shown in Fig. 12.2 and briefly explained in the below section.

12.2.1 Debarking

Debarking is the first step in which fibres are being separated from lignin by the oxidation of chlorine compounds. During debarking, a huge amount of water is added with chemicals and these pulping chemicals are a mixture of lignin and other organic matters (Vepsalainen et al. 2011).

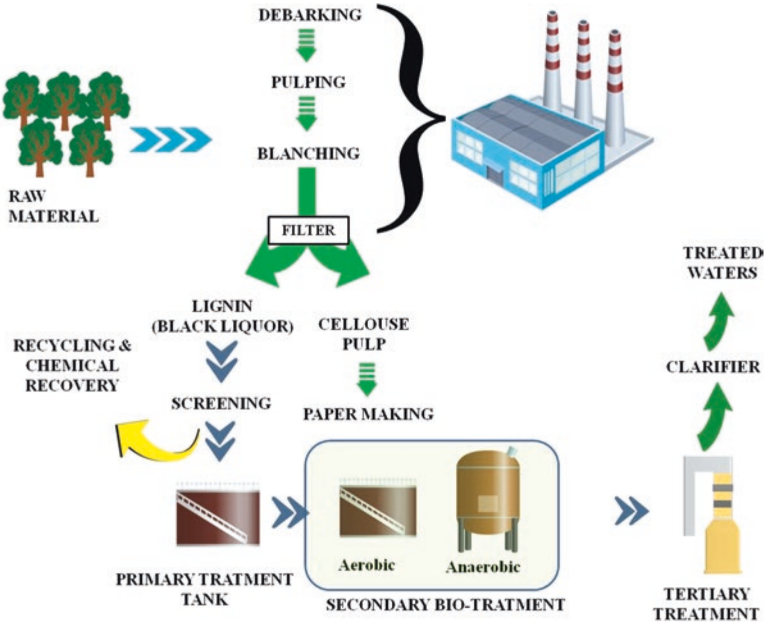


Fig. 12.2 Schematic diagram of processes of pulp and paper making industry

12.2.2 Mechanical Pulping

Mechanical pulp bleaching is different from chemical pulp bleaching. In this process, mechanical force is used to reduce the removal of the lignin and cellulose resulting in low fibre yield. In traditional mechanical pulping process, logs are sent to a revolving stone which grinds it into pulp by rubbing or grinding action. The stone is continuously sprinkled with water for the removal of fibres from the pulping platform as well as to avoid the damages of fibre due to friction on stone which generates the heat. This sprinkled waste is the source of lignin.

12.2.3 Kraft Pulping

Kraft pulping is an alkaline process in which lignin is separated from cellulose and hemi cellulose with white cooking liquor ($NaOH + Na_2S$). Nearly 90–95% of lignin, 50% of hemicellulose and 10% of cellulose are dissolved into the pulp. In this process, molecular weight of the lignin macromolecules decreased due to molecular fracture, and it is dissolved in alkaline solution which makes the black liquor. At present nearly 6.3×10^5 tons of kraft lignin is produced all over the world. This kraft lignin is mainly used for combustion and that shows its low-value utilization.

12.2.4 Sulfite Pulping

It is a pulping process in which lignin is extracted from wood at acidic condition in presence of magnesium bisulfate and excess amount of sulfur dioxide. The sulfite pulping process weakens the fibre due its acidic in nature which gives lower yield of fibre compared to kraft pulping technique. However, it can remove more amount of lignin which is the main advantage of this process.

12.2.5 Paper Making Process

Paper making is a two-step method such as extraction and manufacturing. After the extraction of fibres and separation of lignin from pulp, cellulosic fibres are ready for manufacturing of paper. Then the fibrous pulp is combined with water and placed on paper making equipment where it gets flattened, dried, cut into sheets, roll and packed (Bajpai 2015).

12.3 Existing Treatment Methods for Pulp and Paper Industry Effluent

The paper creation process has two steps: a fibrous raw material from pulping of wood chips is preliminary converted into pulp and then rich cellulosic pulp converted into paper after blanching. As discussed earlier, the paper making process requires a huge amount of water and chemicals. The chemicals and water added in the blanching process are released in the form of black liquor with an enormous amount of kraft lignin which needs to be treated properly (Raj et al. 2014 and Karrasch et al. 2006). In order to treat the pulp and paper effluent, it is very important to determine the contaminants present in the effluent first. Generally three treatment steps are followed for pulp and paper mill effluent in the treatment sectors such as primary, secondary and tertiary treatments. The following section briefly explains each treatment step.

12.3.1 Primary Treatment

Primary treatment plays an important role in removing suspended solids, total heavy partials and other particulate matter of the pulp and paper mill effluent. However floating bark, dust and chopped wood, fibres, other toxic compounds, colloidal particles and its black colours can't be treated by preliminary process (Bhattacharjee et al. 2007). Primary treatment starts with screening process followed by sedimentation; flotation involves chemical treatment, coagulation and flocculation, ozonation and electrolysis using ultraviolet ray ((El-Ashtoukhy et al. 2009; Hogenkamp 1999; Wong et al. 2006; Kishimoto et al. 2010). Heavy solids are allowed to settle at the bottom of primary settling tank. Reactor oil, grease and other lighter solid particles float on the surface of the tank. The settled and floating materials are removed by screening process, and the remaining liquid passes on to the secondary treatment process. Due to the complex structural of lignin, it is very hard to separate/treat the lignin in the primary treatment step. The physicochemical treatment method is commonly used for first degree and third degree of wastewater treatment (Ashrafi et al. 2015).

12.3.2 Secondary Treatment

Most of the pulp and paper industrial wastewater treatment plants use second-degree (i.e. aerobic and anaerobic) biological treatment for the efficient removal of organic contaminants. Aerobic treatment is an easiest technique to operate and its operating cost is comparatively less. Hence, aerobic methods in the form of activated sludge treatment and aerated lagoon are commonly utilized by the pulp and paper industries (Mulligan 2002; Pokhrel and Viraraghavan 2004; Thompson and Forster 2003). Aerobic microbes with ligninolytic activity degrade lignin and its derivatives, dyes and other blanched and chlorinated compounds coming from the pulp and paper mill wastewater (Norris et al. 2000). This method is successfully used to reduce the concentration of BOD, COD and Lignin.

Anaerobic digestion process is another secondary treatment method to treat the sewage sludge and wastewater of pulp and paper mill effluent. Anaerobic method is generally used to treat the highly concentrated effluents. Anaerobic digestion is a sequential process of hydrolysis and acidogenesis where microorganisms degrade the organic matters in the absence of oxygen and produce biogas (Meyer and Edwards 2014). Anaerobic microbes are capable of degrading lignin at different active sides and release different enzymes compared to aerobic strains. Up-flow anaerobic sludge blanket and fluidized bed-type reactors are usually used for the treatment of pulp and paper wastewaters (Chen and Horan 1998).

12.3.3 Tertiary Treatment

Tertiary treatment is third-degree process of any wastewater treatment. This is the step where fine pollutants are removed to purify the water, but the complex compounds like lignin can’t be removed by this method. The industries which are discharging their treated effluent on the river or waterway are mostly adopting the tertiary treatment methods to meet the discharge limits of various pollutants coming from effluent. Many tertiary techniques such as enzymatic degradation, polyelectrolyte cleaning, surface adsorption, (UV) ozonation treatment, closed loop systems, fixed bed reactor with biological film processing, membrane filtration and nitrogen fixation are being used in different industrial waste treatment as per the need to achieve the satisfactory values (Rohella et al. 2001). Pulp and paper mill effluent contains a variety of pollutants at large quantity. Hence, much attention need to be paid while adopting the suitable tertiary treatment to efficiently handle the pulp and paper waste. Among many available tertiary treatment methods, industries most commonly adopt only three methods such as adsorption, membrane filtration and chemical oxidation for wastewater treatment. These methods are briefly discussed in the following section.

12.3.3.1 Adsorption

Adsorption is the method where adsorbents and adsorbate play an important role. In this method, surface accumulation of adsorbates (pollutants) takes place on the adsorbent. Adsorbents can adsorb both organic and inorganic pollutants as per the property. Many adsorbents such as activated charcoal/carbon, fuller clay, coal fly ash, etc. are efficiently used to reduce the high-concentration colour in pulp and paper mill waste (Murthy et al. 1991). Due to the complex nature of lignin, it cannot be removed by adsorption method.

12.3.3.2 Membrane Filtration

In order to remove very fine solid particles, both organic and inorganic, bacteria and viruses membrane filtration is used in the tertiary treatment of pulp and paper industry wastewater without changing their biological and chemical nature (Rashed

2013). In this technique, pollutants/solutes are removed in the form of retentive or permeate with the help of mechanical or chemical sieving of particles at a constant pressure. At the present scenario, either on site or at a common treatment plant membrane filtration is used as a viable technique in many paper mills for treating amount of large water and recovers the byproducts. Indeed, the world's largest tubular. Also, this method is highly efficient in removing colour, heavy metals COD, BOD, salts and TDS of pulp and paper industry effluent (Merrill et al. 2001).

12.3.3.3 Chemical Oxidation

The chemical oxidation method comes under the advanced oxidation process. In this process, transformation of electrons occurs during addition of oxidizing agents. The effluent released from pulp and paper industries includes chromophoric and non-chromophoric pollutants. These pollutants can be treated by photo fenton reactions, photocatalysis, wet oxidation, photo-oxidation and ozonation (Balcioglu and Cecen 1999). Black liquor of the pulp and paper industry can be effectively treated by chemical oxidation and photo-Fenton treatment to achieve the high colour removal efficiency (Perez et al. 2002). Wet-oxidation process helps to enhance the biological degradation of pulp and paper wastes (Verenich et al. 2000; Freire et al. 2000). Lignin can be oxidized chemically by adding H_2O_2 as oxidizing agent to remove many phenolic and aromatic organic compounds during chemical oxidation.

12.4 Treatment of Lignin in the Pulp and Paper Industry Effluent

Two types of treatment methods such as physicochemical and bioremediation are available to handle the lignin waste coming from pulp and paper industrial effluent.

12.4.1 Physicochemical

Chemical and physical processes are used to break the structure of the lignocellulosic material into monomers. Steam explosion at 190 °C to 270 °C is the most suggested technique for lignin degradation (Brodeur et al. 2011). Other methods such as ammonia fibre explosion and liquid explosion are being used for minimizing the lignin strength in the effluent (Kim 2018). Hence, lignin can be effectively treated by the physicochemical techniques, but these can't be specific product oriented.

12.4.2 Bioremediation of Lignin

Bioremediation is an innovative and effective technique in which biodegradation of waste present in pulp and paper effluents takes place in a single step by the microorganisms such as fungi, bacteria, algae and enzymes. These biodegrading microbes can be used in a single form or mixed form and also in combination of two/more different microbes like bacteria and fungi with a synergistic effect (Singhal and Thakur 2009).

The rate of reaction in bioremediation enhances when naturally available microbes isolated from the specific pollutant sites being used. Contaminants and pollutants available in the sites help the microorganisms in the form of nutrients and carbon sources/electron donors to grow and replicate. In case of specific degradation, indigenous microorganisms or genetically modified microbial cultures can be used for some treatment. These microorganisms are releasing specific enzymes with specific character for degradation of selective pollutants with faster degradation and desired product formation.

Recent developments in the biodegradation are focusing on some methods which are low-cost, eco-friendly, easy to operate and adapt the global changes for more attractive and efficient cleaning technology. Some of the conventional methods consist of a combination of physical, chemical, and biological processes. These are being used to remove solids, organic matter and some other nutrients from wastewater. For reduction of BOD and COD in the effluent mostly biological methods are recommended. However, conventional biological processes are not efficient for elimination of colour and non-degradable compounds like lignin. Bioremediation of toxic waste is the control technology that uses microbes to catalyse the depolymerization process of complex organics to transform various toxic chemicals into its simple monomers (Wu et al. 2005; Yang et al. 2008). In bioremediation process, microorganisms use waste pollutants as a substrate for their growth and replication during which they are degrading or transforming the wastes from highly complex structure like lignin into valuable monomers (Iyovo et al. 2010; Surani et al. 2011). Degradation of lignin by various biological means such as fungi, algae and bacteria are show in Fig. 12.3.

12.4.2.1 Algal Bioremediation

Bioremediation by microalgae has gained more attention in the recent years due to the flexible growth of algae. Algae growth and development happens through photosynthesis by using simple sources such as solar light and CO_2. It can be utilized for various processes such as carbon mitigation, biofuel production and bioremediation. This multifunctional nature of microalgae makes it a suitable source for several eco-friendly remedies. Microalgae have the ability to degrade some of the toxic compounds such as heavy metals and kraft lignin waste. For instance, *Microcystis* sp. and *Cyclotella cryptica* can efficiently decolourize and degrade the watery kraft lignin waste and cupper, respectively (Sharma et al. 2014; Kumar et al. 2015). In addition, *Chlorella, Microcystis* and *Chlamydomon* mixed algal strains efficiently remove 70% of AOX (Absorbable Organic Halides) and 80% of kraft lignin in 30 days (Sharma et al. 2014; Chandra and Singh 2012). Both pure and mixed algal cultures are capable of removing 70% of kraft lignin colour within 2 months of inoculation (Hossain and Ismail 2015). Algae efficiently transform its metabolic activity to decolourize the lignin molecules with limited assimilation

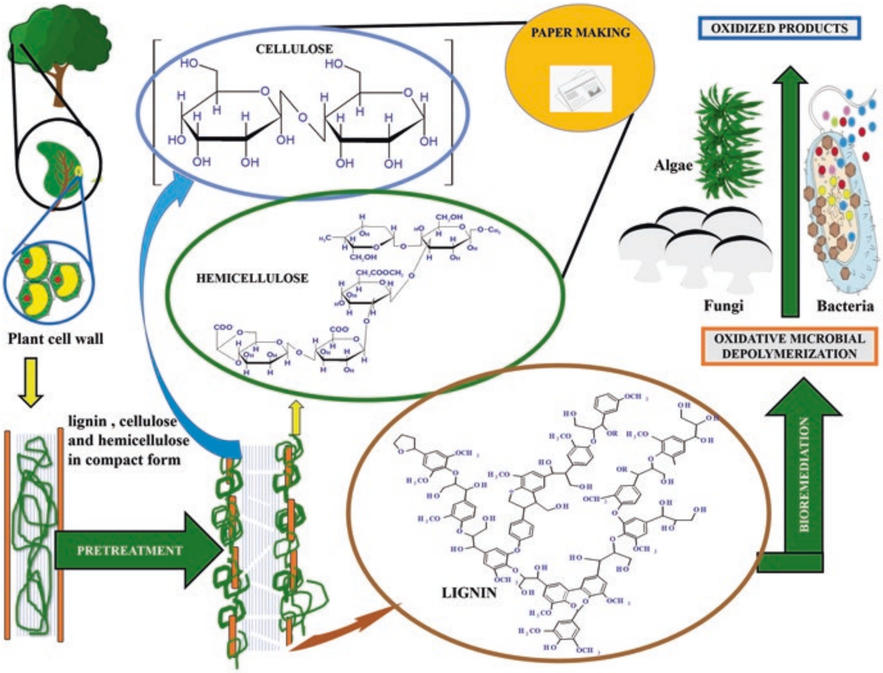


Fig. 12.3 Bioremediation of lignin by various microbes

(Chandra and Singh 2012). Generally, degradation and growth replication of algae is a time-consuming process, and hence, mixed algal strains can give much better degradation results that single culture.

12.4.2.2 Fungal Bioremediation

Fungi are naturally available microorganisms in the soil which take nutrients from the available habitats to grow and replicate easily (Yang et al. 2011). Fungi release extracellular enzymes according to their environment condition which makes their survival easy even at high concentration of any pollutants compared to bacteria (Singhal and Thakur 2009; Kamali and Khodaparast 2015). Among all microorganisms, fungi are most capable of breaking down and degrading the pulp and paper effluent (Rhodes 2013). White-rot fungi are highly proficient for wood as well as lignin degradation. *Schizophyllum commune* white-rot fungus can decolourize the wastewater released from pulp and paper industries (Dashtban et al. 2010). *Tinctoria borbonica*, *Trametes versicolor*, *Phanerochaete chrysosporium* and *Schizophyllum commune* are also capable enough to degrade the lignin and its metabolic compounds and derivative molecules (Rahim and Zaki 2005; Tiku et al. 2010). Similarly, *Trichoderma* spp. and *Aspergillus niger* also effectively degrade the lignin and reduced the dark colour of the effluent released from hardwood pulp bleaching (Dashtban et al. 2010; Kamali and Khodaparast 2015). Fungal cultures also help to reduce the BOD and COD of pulp and paper wastewater (Frostell et al. 1994; Kamali and Khodaparast 2015). A distinct benefit of fungal strains is that compared to all the lignin-degrading microbes, it doesn't require any pretreatment/conditioning for lignin degradation. Carbon and nitrogen not only provide nutrients to microbes but also help improve the lignin degradation efficiency of fungi. Normally, fungal degradation is also a time-consuming process because degradation with fungi is not much effective at the beginning days, but it shows better degradation efficiency after 15–20 days of incubation.

12.4.2.3 Bacterial Bioremediation

Bacterial strains are having ability to degrade lignin and its derivatives into monomers of lignin substructure. Lignin-degrading bacterial strains are called ligninolytic bacteria. There are several ligninolytic bacterial strains reported in the literature for bioremediation of high concentration of lignin coming from pulp and paper industries; among them some are also commercialized (Bugg et al. 2011). Indigenous microbes such as *Bacillus subtilis* and *Micrococcus luteus* are able to substantially reduce the BOD and COD concentration during lignin degradation (Tyagi et al. 2014).

Strains S. *viridosporous* and *Streptomycetes badius*, *Acinetobacter calcoaceticus*, *Pseudomonas putida* and *Pseudomonas aeruginosa* efficiently degrade as well as decolorize the kraft lignin and convert it into the monomers (Ramsay and Nguyen 2002; Rahim and Zaki 2005). *Bacillus cereus* spp. and *Pseudomonas aeruginosa* mixed cultures also effectively decolorize the kraft wastewater (Raj et al. 2007). *Streptomyces viridosporous* and Protozoa are the other mixed cultures isolated from bottom of the lake and used for degradation of kraft lignin as well as its derivatives after the modification (Raj et al. 2007). *Bacillus stearothermophilus T6* is reported as thermophilic and alkali tolerant strain which release enzyme at large scale at the optimum pH 9 and 65 °C. *Enterobacter* spp., *Citrobacter* spp. and *Pseudomonas putida* bacterial strains are highly capable to parallelly reduce the heavy metals, phenolic compounds, sulfate-sulfide substances, COD and BOD while degrading the lignin-rich effluent (Keharia and Madamwar 2003). Although there are many studies available on lignin bioremediation, only few works are reported for a specific product formation which demands for more specific lignin bioremediation studies (Chandra and Bharagava 2013).

12.5 Lignin Degradation Enzyme Assay

Enzymes play an important role in lignin bioremediation process. Microorganisms release specific enzymes during degradation, or synthetically these enzymes are added to the system to bind at the active site and cleave it. In lignin biodegradation, only ligninolytic microbes will release the specific lignin-degrading enzymes such as lignin peroxidase, alkyl aryl etherase, laccase and manganese peroxidase (Chen et al. 2012a). However, these lignin-degrading enzymes can also be added synthetically during the degradation process. When enzymes are added into the pulp and paper mill effluent containing complex lignin, it will smooth the degradation steps of lignin but slow down the product formation (Hossain and Ismail 2015). Lignin degradation is a two-step process where enzymes first catalyse the primary substrate followed by oxidation of a wide range of aromatic compounds. Lignin-degrading enzymes have the potential to reduce a load of organic compounds. Especially, in pulp and paper industrial effluent treatment, these enzymes are very effective in degradation during shock loading. Peroxidase enzymes are more important for colour removal in pulp and paper mill waste which oxidizes effluent and removes colour from wastewater (Gao et al. 2013). The details of lignin-degrading enzymes produced by ligninolytic microbes are disused in the following section.

12.5.1 Lignin Peroxidase (LiP) Assay

Lignin peroxidase is an enzyme which is the first and main enzyme responsible for lignin bioremediation. It contains heme [Fe]-protein of glycosylated enzyme which has high redox potential than other peroxidase. This supports to cleave C-C bonds and oxidize the nonphenolic (b-O-4 linked arylglycerol b-aryl ethers) as well as phenolic structure of lignin (syringic acid, guaiacol, catechol, vanillyl alcohol, acetosyringone) without any mediator (Hofrichter et al. 2010; Sugano 2009). The initial oxidation of the enzymes takes place by H_2O_2 in catalytic cycle to form intermediate and mineralize the recalcitrant aromatic compounds where water molecules are released (Fig. 12.4). Also, LiP's are the enzymes commonly released by various fungal and bacterial strains (Choinowski et al. 1999).

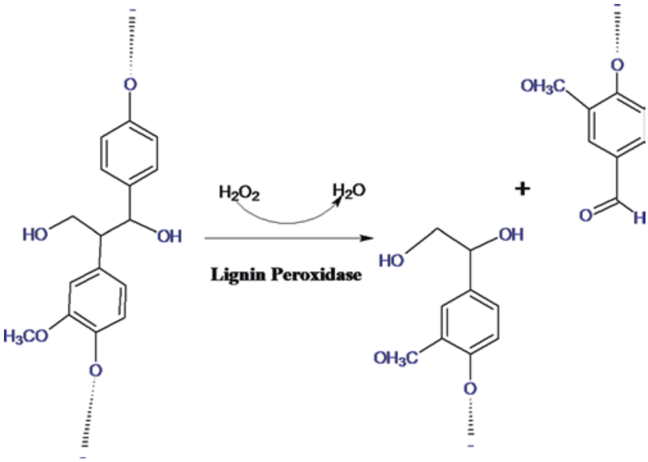


Fig. 12.4 Lignin peroxidase mechanism

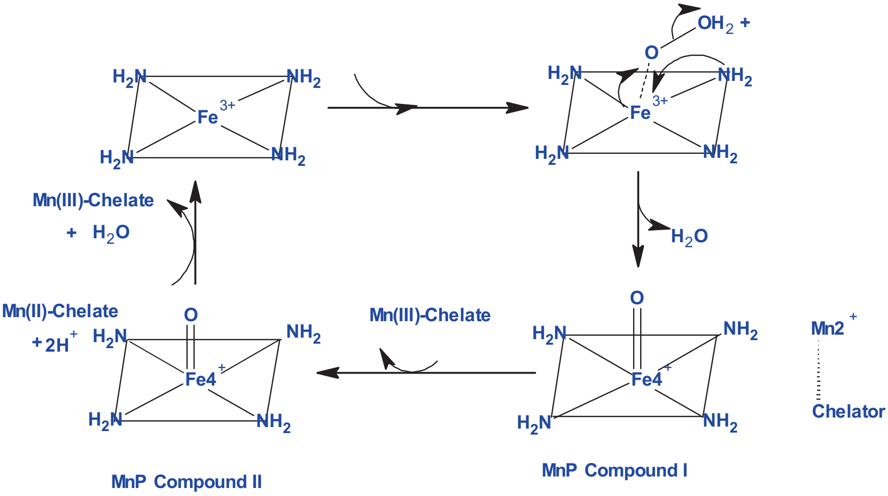


Fig. 12.5 Manganese lignin peroxidase mechanism

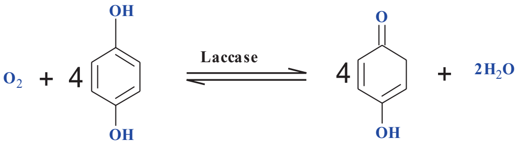
12.5.2 Manganese Peroxidase (MnP) Assay

Manganese peroxidase is another extracellular glycosylated heme protein in which Mn^{2+} act as electron donor. It is being produced by fungi and few bacteria strains (Gaur et al. 2018). MnP plays an important role throughout preliminary stage of lignin digestion (Datta et al. 2017). MnP also needed H_2O_2 for initial oxidation of lignin but it is different mechanism from LnP. MnP oxidizes aromatic structure of lignin by converting Mn^{2+} into Mn^{3+} (Fig. 12.5). The high concentration of Mn^{3+} (III) gives more possibility for treatment of lignin and its derivatives into the wastewater (Mishra and Wimmer 2017). Recently MnP is getting more attention by the researchers due to its high redox potential as compared to laccase for more lignin degradation (Ten and Teunissen 2001; Furukawa et al. 2014).

12.5.3 Laccase Assay

Laccase (Lac) are polyphenol oxidases comprised four copper ions in three different active sites (Fig. 12.6), (Chen et al. 2012b). These assist biodegradation of phenolic substances through the catalysation of one electron substrate oxidation with four-electron reduction of molecular oxygen to water. Laccase oxidizes phenolic units of

Fig. 12.6 Laccase mechanism



lignin and also non-phenolic substrates with the help of certain axillary substrates. Laccase (Lac) enzyme activity can be assayed using Tannic acid and α-Napthol as substrates. Laccase activity has been found in many bacteria and fungi including non-ligninolytic members, many plants and insects (Soden, et al. 2002). Laccases are very attractive biocatalysts in industries because they are different from other oxidases, do not produce toxic H_2O_2 and don't need any other cofactors. Therefore other than lignin degradation, laccases are used for many industrial applications such as production of fine chemicals and pharmaceuticals, treatment of industrial wastewaters and stabilization of beverages and improve the organoleptic properties in food industries (De Gonzalo et al. 2016).

12.6 Factors Affecting the Degradation Process

Specific conditions are required for effective degradation of organic and inorganic compounds in the effluent. Lignin is discharged at high concentration in the form of black liquor from pulp and paper industries. Therefore, the process parameters such as selection of bacteria/fungi strains, pH, temperature of the waste matter, supplementary carbon source, mixing speed, shock loading, seed inoculum size and design of treatment reactor are highly important for efficient degradation and decolourization of lignin. pH is an important factor considered for the optimum growth of microorganisms. Lignin is a basic compound and its pH is varying from 9 to 13. Colour concentration of effluent increases the pH up to 10.0 (Tiku et al. 2010). However, pH of the pulp and paper effluents are usually dropped up to pH 2.0 during the sedimentation process of effluent treatment. Reduction of colour and turbidity level in pulp and paper effluent is achieved by the precipitation of negatively charged lignin compounds and its derivatives. Also, colour removal efficiency increases while adding the carbon source (glucose and sucrose) during bioremediation (Datta et al. 2017). The size of inoculum plays a significant role in microbial degradation or decolourization of lignin and its derivatives due to different biomass ratio present in the inoculum. *Bacillus* spp. with 1% of inoculum size at a fixed rate of carbon source gives efficient result by degrading monomers of the lignin (Chandra et al. 2009). Shaking/mixing speed generally followed in the range of 50–200 rpm to give the better results (Hossain and Ismail 2015). Thus, the selection of correct process parameters is very important in bioremediation process to achieve the expected and efficient results.

12.7 Conclusion

Bioremediation is an efficient, economical and successful approach to clean industrial effluents at the present scenario. Microbes present in the pulp and paper effluents could be used as naturally available and very effective source for lignin degradation in addition to other indigenous microbes. Microbes can degrade three major lignocellulosic materials such as cellulose, hemicellulose and bulk amount of lignin as well as its derivatives present in the pulp and paper mill effluent. The usage of hybrid techniques make the treatment processes more efficient. Most of the available reports/studies ensure that biological treatment of pulp and paper industry effluent by a variety of fungal and bacterial strains are highly efficient. The other conventional physicochemical treatment methods are highly expensive, and those methods are not effective and feasible to remove the variety of pollutants such as high molecular weight compounds, chlorinated lignins, toxicants, suspended solids, colour and high BOD and COD present in the pulp and paper mill effluent. Among various conditions in bioremediation, aerobic condition is more effective to degrade different types of pollutants present in the pulp and paper industries. But anaerobic condition is not an appropriate method for kraft lignin degradation due to its more toxicity to the anaerobic microbes. Hence, for the degradation of lignin, aerobic treatment is highly recommended. Among different microbes, fungi and bacteria with efficient enzyme activity are found to be more suitable and efficient for bioremediation of lignin at optimum nutrient and operating conditions to achieve superior discharge standard.

Acknowledgments The authors would like to thank Science and Engineering Research Board (DST), Govt. of India for allowing the authors to use the project (ECR/2016/000435) related information to make this chapter.

References

Ashrafi O, Yerushalmi L, Haghighat F (2015) Wastewater treatment in the pulp-and-paper industry: a review of treatment processes and the associated greenhouse gas emission. J Environ Manag 158:146–157

Bajpai P (2015) Basic overview of pulp and paper manufacturing process. In: Green chemistry and sustainability in pulp and paper industry. Springer, Cham, pp 11–39

Balcioglu IA, Cecen F (1999) Treatability of Kraft pulp bleaching wastewater by biochemical and photocatalytic oxidation. Water Sci Technol 40(1):281–288

Bhattacharjee S, Datta S, Bhattacharjee C (2007) Improvement of wastewater quality parameters by sedimentation followed by tertiary treatments. Desalination 212(1–3):92–102

Brodeur G, Yau E, Badal K, Collier J, Ramachandran KB, Ramakrishnan S (2011) Chemical and physicochemical pretreatment of Lignocellulosic biomass: a review. J Enzym Res 2011:1–17

Bruijnincx PC, Rinaldi R, Weckhuysen BM (2015) Unlocking the potential of a sleeping giant: lignins as sustainable raw materials for renewable fuels, chemicals and materials. Green Chem 17(11):4860–4861

Bugg TDH, Ahmad M, Hardiman EM, Rahmanpour R (2011) Pathways for degradation of lignin in bacteria and fungi. Nat Prod Rep 28(12):1883–1896

Chandra R, Bharagava RN (2013) Bacterial degradation of synthetic and Kraft lignin by axenic and mixed culture and their metabolic products. J Environ Biol 34(6):991

Chandra R, Singh R (2012) Decolourisation and detoxification of rayon grade pulp paper mill effluent by mixed bacterial culture isolated from pulp paper mill effluent polluted site. Biochem Eng J 61:49–58

Chandra R, Raj A, Yadav S, Patel DK (2009) Reduction of pollutants in pulp paper mill effluent treated by PCP-degrading bacterial strains. Environ Monit Assess 155:1–11

Chaudhry S, Paliwal R (2018) Techniques for remediation of paper and pulp mill effluents: processes and constraints. In: Handbook of environmental materials management. Springer International Publishing, Cham

Chen W, Horan NJ (1998) The treatment of a high strength pulp and paper mill effluent for wastewater re-use. Environ Technol 19(2):173–182

Chen HW, Hsu CH, Hong GB (2012a) The case study of energy flow analysis and strategy in pulp and paper industry. Energy Policy 43:448–455

Chen Y, Sarkanen S, Wang YY (2012b) Lignin-degrading enzyme activities. Biomass Conversion 908:251–268

Choinowski T, Blodig W, Winterhalter KH, Piontek K (1999) The crystal structure of lignin peroxidase at 1.70 Å resolution reveals a hydroxy group on the Cβ of tryptophan 171: a novel radical site formed during the redox cycle. J Mol Biol 286(3):809–827

Dashtban M, Schraft H, Syed TA, Qin W (2010) Fungal biodegradation and enzymatic modification of lignin. Int J Biochem Mol Biol 1(1):36

Datta R, Kelkar A, Baraniya D, Molaei A, Moulick A, Meena R, Formanek P (2017) Enzymatic degradation of lignin in soil: a review. Sustainability 9(7):1163

De Gonzalo G, Colpa DI, Habib MHM, Fraaije MW (2016) Bacterial enzymes involved in lignin degradation. J Biotechnol 236:110–119

Dos Santos Abreu H, do Nascimento AM, Maria MA (2007) Lignin structure and wood properties. Wood Fiber Sci 31(4):426–433

El-Ashtoukhy ES, Amin NK, Abdelwahab O (2009) Treatment of paper mill effluents in a batch-stirred electrochemical tank reactor. Chem Eng J 146(2):205–210

El-Rahim WA, Zaki EA (2005) Functional and molecular characterization of native Egyptian fungal strains capable of removing textile dyes. Arab J Biotechnol 8(2):189–200

Freire RS, Kunz A, Duran N (2000) Some chemical and toxicological aspects about paper mill effluent treatment with ozone. Environ Technol 21(6):717–721

Frostell B, Boman B, Ek M, Palvall B, Berglund M, Lindström A (1994) Influence of bleaching conditions and membrane filtration on pilot scale biological treatment of Kraft mill bleach plant effluent. Water Sci Technol 29(5–6):163–176

Furukawa T, Bello FO, Horsfall L (2014) Microbial enzyme systems for lignin degradation and their transcriptional regulation. Front Biol 9(6):448–471

Gao J, Xu G, Qian H, Liu P, Zhao P, Hu Y (2013) Effects of nano-TiO2 on photosynthetic characteristics of Ulmus elongata seedlings. Environ Pollut 176:63–70

Gaur N, Narasimhulu K, Pydisetty Y (2018) Biochemical and kinetic characterization of laccase and manganese peroxidase from novel Klebsiella pneumoniae strains and their application in bioethanol production. RSC Adv 8(27):15044–15055

Higuchi T (1990) Lignin biochemistry: biosynthesis and biodegradation. Wood Sci Technol 24(1):23–63

Hofrichter M, Ullrich R, Pecyna MJ, Liers C, Lundell T (2010) New and classic families of secreted fungal heme peroxidases. Appl Microbiol Biotechnol 87(3):871–897

Hogenkamp H (1999) Flotation: the solution in handling effluent discharge. PAPER ASIA 15(2):16–18

Hossain K, Ismail N (2015) Bioremediation and detoxification of pulp and paper mill effluent: a review. Res J Environ Toxicol 9(3):113–134

Iyovo GD, Du G, Chen J (2010) Sustainable bioenergy bioprocessing: biomethane production, digestate as biofertilizer and as supplemental feed in algae cultivation to promote algae biofuel commercialization. J Microb Biochem Technol 2(4):100–106

Kamali M, Khodaparast Z (2015) Review on recent developments on pulp and paper mill wastewater treatment. Ecotoxicol Environ Saf 114:326–342

Karrasch B, Parra O, Cid H, Mehrens M, Pacheo P, Urrutia R, Valdovinos C, Zaror C (2006) Effects of pulp and paper mill effluents on the microplankton and microbial self-purification capabilities of the Biobio river. Chile. Sci Total Environ 359:194–208

Keharia H, Madamwar D (2003) Bioremediation concepts for treatment of dye containing wastewater: a review. Indian J Exp Biol 41(09):1068–1075

Kim D (2018) Physico-chemical conversion of lignocellulose: inhibitor effects and detoxification strategies: a mini review. Molecules 23(2):309

Kishimoto N, Nakagawa T, Okada H, Mizutani H (2010) Treatment of paper and pulp mill wastewater by ozonation combined with electrolysis. J Water Environ Technol 8(2):99–109

Kumar KS, Dahms HU, Won EJ, Lee JS, Shin KH (2015) Microalgae-a promising tool for heavy metal remediation. Ecotoxicol Environ Saf 113:329–352

Merrill DT, Maltby CV, Kahmark K, Gerhardt M, Melecer H (2001) Evaluating treatment process to reduce metals concentrations in pulp and paper mill wastewaters to extremely low values. TAPPI J 84(4):52

Meyer T, Edwards EA (2014) Anaerobic digestion of pulp and paper mill wastewater and sludge. Water Res 65:321–349

Mishra PK, Wimmer R (2017) Aerosol assisted self-assembly as a route to synthesize solid and hollow spherical lignin colloids and its utilization in layer by layer deposition. Ultrason Sonochem 35:45–50

Moreira PR, Duez C, Dehareng D, Antunes A, Almeida-Vara E, Frère JM, Duarte J (2005) Molecular characterisation of a versatile peroxidase from a Bjerkandera strain. J Biotechnol 118(4):339–352

Mulligan CN (2002) Environmental biotreatment: Technologies for air. Water. In: Soil and wastes. Government Institutes, Rockville

Murthy BSA, Sihorwala TA, Tilwankar HV, Killedar DJ (1991) Removal of colour from pulp and paper mill effluents by sorption technique—a case study. Indian J Environ Prot 11(5):360

Norris P, Marshall R, Richard M (2000) High temperature effects on activated sludge treatment performance and sludge quality in a recycle mill. In: 2000 TAPPI international environmental conference and exhibition, pp 383–388

Perez M, Torrades F, Domenech X, Peral J (2002) Treatment of bleaching Kraft mill effluents and polychlorinated phenolic compounds with ozonation. J Chem Technol Biotechnol: Int Res Process Environ Clean Technol 77(8):891–897

Pokhrel D, Viraraghavan T (2004) Treatment of pulp and paper mill wastewater-a review. Sci World J 333(1–3):37–58

Rahmanpour R, Bugg TD (2015) Characterisation of Dyp-type peroxidases from Pseudomonas fluorescens Pf-5: oxidation of Mn (II) and polymeric lignin by Dyp1B. Arch Biochem Biophys 574:93–98

Raj A, Chandra R, Reddy MMK, Purohit HJ, Kapley A (2007) Biodegradation of Kraft lignin by a newly isolated bacterial strain, Aneurinibacillus aneurinilyticus from the sludge of a pulp paper mill. World J Microbiol Biotechnol 23(6):793–799

Raj A, Kumar S, Haq I, Singh SK (2014) Bioremediation and toxicity reduction in pulp and paper mill effluent by newly isolated ligninolytic Paenibacillus sp. Ecol Eng 71:355–362

Rajwar D, Paliwal R, Rai JPN (2017) Biodegradation of pulp and paper mill effluent by co-culturing ascomycetous fungi in repeated batch process. Environ Monit Assess 189(9):482

Ramsay JA, Nguyen T (2002) Decoloration of textile dyes by Trametes versicolor and its effect on dye toxicity. Biotechnol Lett 24(21):1757–1761

Rashed MN (2013) Adsorption technique for the removal of organic pollutants from water and wastewater. In: Organic pollutants-monitoring, risk and treatment. IntechOpen

Rhodes CJ (2013) Applications of bioremediation and phytoremediation. Sci Prog 96(4):417–427

Rohella RS, Choudhury S, Manthan M, Murty JS (2001) Removal of colour and turbidity in pulp and paper mill effluents using polyelectrolytes. Indian J Environ Health 43(4):159–163

Savant DV, Abdul-Rahman R, Ranade DR (2006) Anaerobic degradation of adsorbable organic halides (AOX) from pulp and paper industry wastewater. Bioresour Technol 97(9):1092–1104

Sharma R, Chandra S, Singh A, Singh K (2014) Degradation of pulp and paper mill effluents. IIOAB J 5(3):6–12

Singhal A, Thakur IS (2009) Decolourization and detoxification of pulp and paper mill effluent by Cryptococcus sp. Biochem Eng J 46(1):21–27

Soden DM, O'callaghan J, Dobson ADW (2002) Molecular cloning of a laccase isozyme gene from Pleurotus sajor-caju and expression in the heterologous Pichia pastoris host. Microbiology 148(12):4003–4014

Su Y, Yu X, Sun Y, Wang G, Chen H, Chen G (2018) Evaluation of screened lignin-degrading fungi for the biological pretreatment of corn Stover. Sci Rep 8(1):5385

Sugano Y (2009) DyP-type peroxidases comprise a novel heme peroxidase family. Cell Mol Life Sci 66(8):1387–1403

Surani JJ, Akbari VG, Purohit MK, Singh SP (2011) PAH base, a freely available functional database of polycyclic aromatic hydrocarbons (PAHs) degrading bacteria. J Bioremed Biodegr 2(1):116

Ten Have R, Teunissen PJ (2001) Oxidative mechanisms involved in lignin degradation by white-rot fungi. Chem Rev 101(11):3397–3414

Thompson G, Forster C (2003) Bulking in activated sludge plants treating paper mill wastewaters. Water Res 37(11):2636–2644

Tiku DK, Kumar A, Chaturvedi R, Makhijani SD, Manoharan A, Kumar R (2010) Holistic bioremediation of pulp mill effluents using autochthonous bacteria. Int Biodeterior Biodegradation 64(3):173–183

Tyagi S, Kumar V, Singh J, Teotia P, Bisht S, Sharma S (2014) Bioremediation of pulp and paper mill effluent by dominant aboriginal microbes and their consortium. Int J Environ Res 8(3):561–568

Vepsalainen M, Kivisaari H, Pulliainen M, Oikari A, Sillanpaa M (2011) Removal of toxic pollutants from pulp mill effluents by electrocoagulation. Sep Purif Technol 81(2):141–150

Verenich S, Laari A, Kallas J (2000) Wet oxidation of concentrated wastewaters of paper mills for water cycle closing. Waste Manag 20(4):287–293

Wong SS, Teng TT, Ahmad AL, Zuhairi A, Najafpour G (2006) Treatment of pulp and paper mill wastewater by polyacrylamide (PAM) in polymer induced flocculation. J Hazard Mater 135(1–3):378–388

Wu J, Xiao YZ, Yu HQ (2005) Degradation of lignin in pulp mill wastewaters by white-rot fungi on biofilm. Bioresour Technol 96(12):1357–1363

Yang C, Cao G, Li Y, Zhang X, Ren H, Wang X, Xu P (2008) A constructed alkaline consortium and its dynamics in treating alkaline black liquor with very high pollution load. PLoS One 3(11):3777

Yang Q, Angly FE, Wang Z, Zhang H (2011) Wastewater treatment systems harbor specific and diverse yeast communities. Biochem Eng J 58:168–176

13 Bioremediation of Chromium Using a Laboratory-Scale Sand Bed Reactor

Priyanka Khan, Kanay Pujara, S. Murugavelh, and K. Mohanty

Abstract

Cr(VI) reduction was performed in a sand bed reactor loaded with indigenous bacterial strain. Enrichment of the bacterial strains isolated from different locations of chromium-contaminated sites at Ranipet, Vellore district of Tamil Nadu. Molasses was used as the substrate for bacterial growth to provide economic viability. The optimum concentration of molasses and bacterial concentration were found to be 60 mg/g of soil and 15 mg/g of soil, respectively. Maximum Cr(VI) reduction potential was reported for the strain isolated from the highly contaminated location. At higher initial concentration, bioreduction of Cr(VI) started after 120 h. The sand bioreactor was packed with 1800 g of Cr(VI)-contaminated sand, and the total chromium was estimated to be 4460 mg/g of soil. The Cr(VI) present in the bioreactor was reduced to near zero after 24 days of study. The percentage of Cr(VI) reduction to Cr(III) was observed to be 97.9%. The specific Cr(VI) reduction was found to be higher for higher Cr(VI) concentration. Sand bed reactor is a viable, environmental friendly technology for bioremediation of Cr(VI).

P. Khan
School of Civil Engineering, VIT, Vellore, Tamil Nadu, India

K. Pujara
School of Chemical Engineering, VIT, Vellore, Tamilnadu, India

S. Murugavelh
CO2 Research and Green Technologies Centre, VIT, Vellore, Tamil Nadu, India

K. Mohanty (✉)
Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati, Assam, India
e-mail: kmohanty@iitg.ac.in

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_13

Keywords
Cr(VI) · Sand bed reactor · Molasses · Performance evaluation · Kinetics

13.1 Introduction

Electroplating, leather tanning, textile dyeing, metal processing, and wood preservation industries utilize chromium in larger proportion. Chromium acts as an essential nutrient for growth and metabolic activities of microorganisms at lower concentrations. Higher concentration of chromium leads to cell inhibition in microbes. Chromium can be found in the environment in two oxidation states, Cr(VI) and Cr(III). The mutagenic and carcinogenic nature of Cr(VI) renders it more toxic (Bailey and Ollis 1986). Extensive industrial activity leads to surge in chromium effluent discharge (Boop and Elrich 1988). The USEPA has set a maximum contaminant level for Cr(VI) in domestic water at 0.05 mg L^{-1} (APHA 1994). Conventional methods used for the removal of Cr(VI) include chemical reduction to its trivalent form, sorption onto ion exchange resins and biological materials, precipitation, membrane separation, etc. (Viamjala et al. 2003). The use of chemicals generates a huge amount of chemical sludge, and the ion exchange is a very costly process (Liu et al. 2006). The search for a new technology has resulted in the innovation of biological process for the reduction of Cr(VI). Microorganisms have developed the capability to survive under heavy metal load by reducing the toxicity of the metals. Microbial reduction of Cr(VI) to Cr(III) is a suitable alternative for the conventional physicochemical methods. The advantage of the microbial reduction of Cr(VI) is that it can reduce relatively lower concentrations of Cr(VI) which cannot be treated by other methods (Wang and Shen 1997).

A wide range of bacteria are reported in literature for the reduction of Cr(VI). Shen and Wang (1992) reported complete reduction of Cr(VI) at an initial concentration of 27 mg L^{-1} by *E.* coli. Wang and Shen (1997) studied the reduction of Cr(VI) by *Bacillus* sp. and *Pseudomonas fluorescens* LB 300 and reported 100% and 90% reduction, respectively, for an initial concentration of 27 mg L^{-1} of Cr(VI). Liu et al. (2006) used *Bacillus* sp. for the reduction of Cr(VI) in the presence of glucose as a substrate for growth; a maximum of 87.5% reduction of Cr(VI) was obtained with an initial Cr(VI) concentration of 40 mg L^{-1}. During the bioreduction process, Cr(VI) acts as an electron acceptor (Xu et al. 2011). Microbial reduction of Cr(VI) can be attained directly by microbial metabolism or by bacterial metabolites such as enzymes. Cr(VI) reduction can be achieved with soluble reductase produced during the reduction studies (Cronje et al. 2011). The production of the soluble reductase by the bacteria is a cometabolism process and hence does not generate biochemical energy to support growth (Liu et al. 2010). The reduction of Cr(VI) by the enzymes is not substrate specific for Cr(VI) (Philip et al. 1998). Previous studies on Cr(VI) reduction using CFE extracts have reported NADH and NADPH as electron donors (Eckenfedler 1989; Chen and Hao 1997).

In the present work, molasses is used as a carbon source for the growth and reduction of the Cr(VI) by isolated from waste soil. The role of pH, temperature, and initial Cr(VI) concentration on Cr(VI) reduction was reported.

13.2 Materials and Methods

13.2.1 Cr(VI) Stock Solution

A Cr(VI) stock solution was prepared by dissolving 2.82 g of $K_2Cr_2O_7$ in 1000 mL deionized water, shaking it at 150 rpm for 15 min to get complete dissolution. Cr(VI)-spiked medium was prepared by diluting this solution to required concentration in the growth media.

13.2.2 Soil Sample

10 kg of soil samples were collected from a contaminated site located at Ranipet, Tamil Nadu, India, in sterile bags. The soil samples were sieved to remove the boulders. The soil samples were dried at 60 C for 24 h in a hot air oven. The dried samples were characterized as per standard procedure (APHA 1994). The soil characteristics are given in Table 13.1.

13.2.3 Bacterial Growth Media

The nutrient medium for bacterial growth consisted of peptone 10 g, beef extract 2 g, molasses 1 g, and sodium chloride 5 g in 1 l of distilled water, and the mineral medium (M1) consisted of K_2HPO_4 2.12 g, H_2PO_4 2.12 g, NaCl 2 g, $MgSO_4 \cdot 7H_2O$ 1 g, $CaCl_2$ 0.1 g, and KNO_3 4 g in 1 l of distilled water. The pH was maintained at 7 ± 0.2 by using HCl or NaOH. Molasses was used as a carbon source. Sterilized media were used for all the studies.

Table 13.1 Characteristics of the soil used in the bioreactor

Soil organic matter	6.5 ± 0.5%
Cr(VI)	2.5–5.5 mg/g of soil
Total chromium	9 ± 12 mg/g of soil
Coefficient of curvature	1.067
Uniformity coefficient	6.67
pH	8
Sand	46 ± 1.5%
Silt	23 ± 1%
Clay	6 ± 0.3%

13.2.4 Sand Bed Reactor

A 3-mm-thick acrylic transparent sheet was used for the fabrication of the reactor. Four sample collection ports were provided at 5, 10, 15, and 20 cm from the top section of the reactor. The diameter and height of the reactor were 10 cm and 25 cm, respectively. A leachate tank was provided at the bottom compartment, 12 cm in diameter and 10 cm in height, to collect the effluent from the bioreduction process. Gravel, glass beads, and sand were packed to a height of 4.5 cm as filter media (Fig. 13.1). 3 kg of the contaminated soil was loosely packed to a height of 18 cm. The reactor was supplied with molasses, nutrient media, and enriched microorganisms along with contaminated soil to augment the bioreduction process. Cr(VI) concentrations in the leachate were analyzed periodically. The top of the reactor was covered with wet cotton to maintain the moisture content.

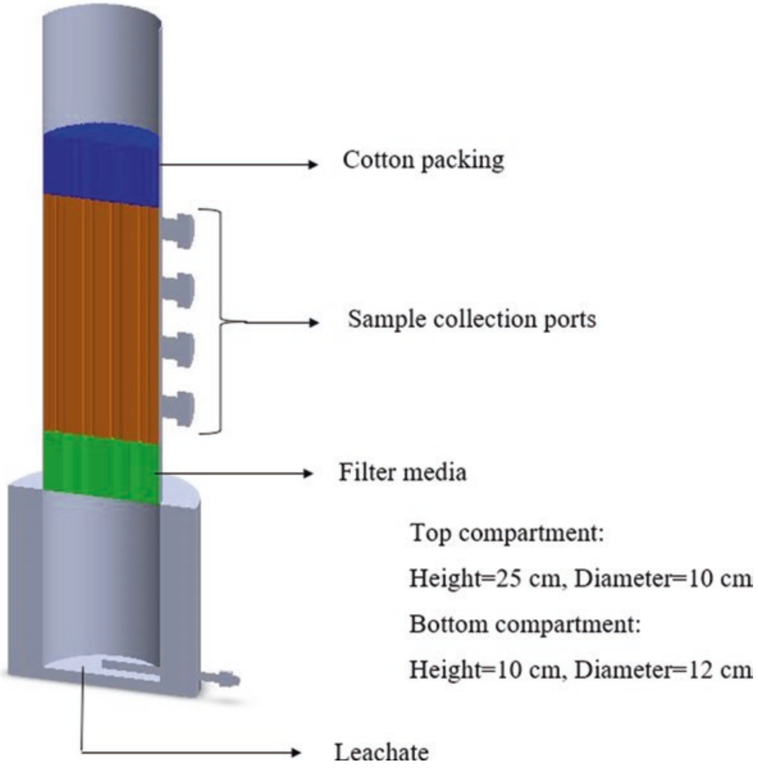


Fig. 13.1 Cross-sectional view of the sand bed reactor

13.3 Results and Discussion

13.3.1 Bioreduction Experiments

The factors affecting the growth and bioreduction were investigated in a sand bed reactor with 100 mL of Cr(VI)-spiked medium for 48 h. The studies on optimizing pH were performed at 37 °C with an initial glucose concentration of 1 g L^{-1}. The bioreduction media was prepared with different pH ranging from 1 to 8 for various concentrations of Cr(VI). The solution pH was measured using a pH meter (Sartorius AG 37070 Goettingen, Germany). At pH 1, 2, and 3, formation of Cr(III) occurred naturally due to the acidic environment. The Cr(III) thus formed was oxidized using potassium permanganate to convert Cr(III) to Cr(VI) [15]. Experiments were performed to study optimal concentration of carbon source, glucose, on the growth and reduction of Cr(VI). The bioreduction media with an initial Cr(VI) concentration of 40 mg L^{-1} was prepared by varying the concentration of glucose between 250 mg L^{-1} and 2000 mg L^{-1}. Samples were taken at specific time intervals (1 h) and centrifuged at 12000 X g; the biomass concentration was measured as OD $_{600}$. The concentration of Cr(VI) was measured spectrophotometrically using diphenyl carbazide (DPC) at 540 nm using a UV spectrophotometer (Perkin Elmer, Model Lambda 35). Interference of growth was eliminated using calibration curves obtained with the same medium. Total Cr concentration was measured by atomic absorption spectrophotometer (Varian AA240 FS).

The influence of Cr(VI) on reduction was studied by varying Cr(VI) concentration from 10 mg L^{-1} to 40 mg L^{-1}. Glucose at an initial concentration of 1 g L^{-1} was used as a sole carbon source. pH was maintained at 7. The flasks containing the bioreduction media with various concentrations of Cr(VI) were inoculated with a loopful of overnight-grown cultures of *enriched bacteria*. The flasks were incubated in an incubator shaker (Daihan LabTech Co Ltd., Model LSI 3016 –R) at 37 °C and 180 rpm. Samples were withdrawn aseptically at regular time intervals of 3 h and centrifuged at 15000 × g for 15 min, and the supernatant was used for metal analysis. A part of the supernatant was used for the analysis of total Cr, and another part of the supernatant was used for the analysis of Cr(VI). Bioreduction was reported as the change in the concentration of Cr(VI) to Cr(III) at regular time intervals.

13.3.2 Effect of Molasses on the Reduction of Cr(VI)

The growth media for the enriched bacterial culture was modified by adding molasses as a carbon source. Studies were conducted to determine the amount of molasses required for the reduction of Cr(VI) (Fig. 13.2). Molasses supplements the growth of the bacteria. It was observed that 15 mg L^{-1} of molasses was essential for the reduction of Cr(VI) by the enriched *bacterial strains* (Fig. 13.2). Cr(VI) reduction decreased with molasses concentrations exceeding 15 mg L^{-1}. It was also observed that the reduction of Cr(VI) decreased when the concentration of molasses was decreased below 5 g L^{-1}. The decrease in Cr(VI) reduction at concentration above and below 15 mgL^{-1} of molasses was due to the nonavailability of the free

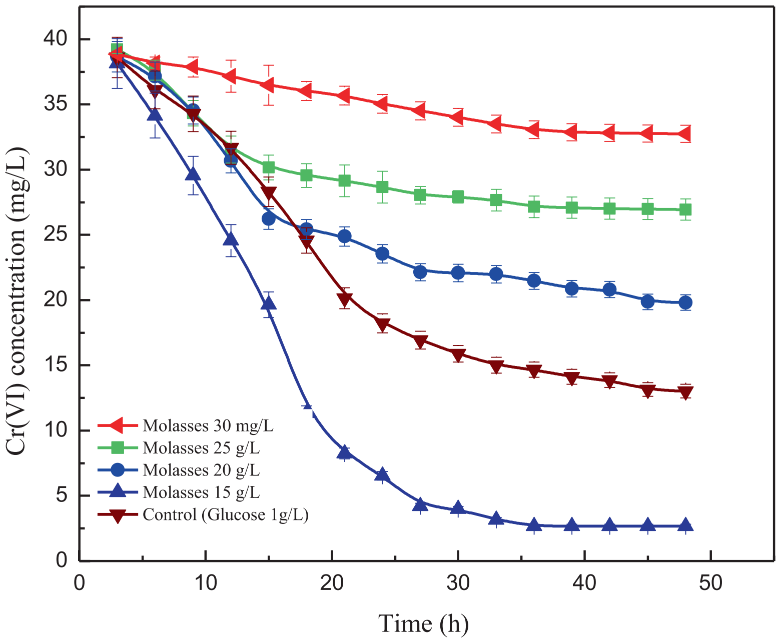


Fig. 13.2 Effect of molasses on bioreduction of chromium

amino acids which also acts as electron donors for the Cr(VI) reduction at lower concentration and substrate inhibition at higher concentration.

13.3.3 Effect of Initial Cr(VI) Concentration on the Reduction of Cr(VI)

The effect of initial Cr(VI) ions on the reduction process was evaluated. The concentration of the Cr(VI) varied between 10 and 50 mg L^{-1} in the reduction media. It was observed that the Cr(VI) concentration decreased from initial concentration of 10, 20, and 30 mg L^{-1} to near zero (Fig. 13.3). The reduction obtained with an initial concentration of 50 mg L^{-1} of Cr(VI) was insignificant (61%) when compared with the other concentrations studied. 10, 20, 30, and 40 mg L^{-1} of initial concentration of Cr(VI) in the media resulted in 98.6, 96.3, 94.4, and 93.3% of Cr(VI) reduction, respectively. The decreased reduction in the Cr(VI) concentration for an initial concentration beyond 40 mg L^{-1} was due to the toxicity of the Cr(VI) on *bacterial strains* at higher concentrations. It was observed that the organism was able to reduce Cr(VI) to near-zero level for concentrations ranging up to 40 mg L^{-1}.

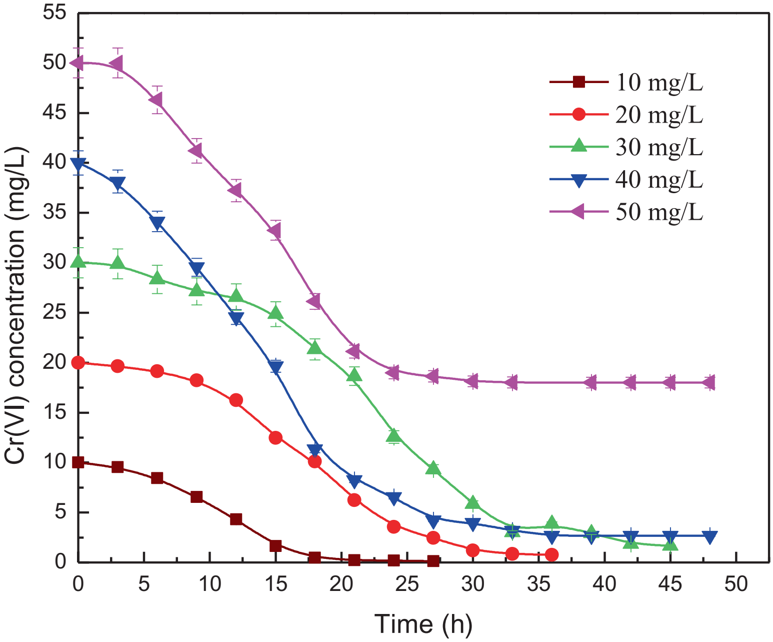


Fig. 13.3 Effect of initial chromium concentration on bioreduction

13.3.4 Effect of pH on the Reduction of Cr(VI)

The pH of a solution is an important parameter for any wastewater treatment process. pH of the media affects solubility of Cr(VI) and the growth of the bacteria. Bioreduction of Cr(VI) was studied for a wide range of pH (1–7). The reduction of Cr(VI) was found to be dependent on the pH of the growth media. It was observed that the maximum reduction of 98.6% was obtained with an initial concentration of 10 mg L^{-1} at pH 7 (Fig. 13.4). The decrease in the reduction on either side of this pH range was due to the fact that the pH affected the growth of the organism. The growth of the bacteria was affected at acidic pH as the organism was adapted to grow initially under pH 7. As the pH of the media was modified, the growth was affected which had a significant effect on the metabolism and the Cr(VI) reduction by *enriched bacterial culture*. At acidic pH(1–4), the cells disintegrated, resulting in the loss of their metabolic activity. pH 6 and 7 favored the growth and bioreduction of Cr(VI). At pH 6 and 7, the cells were intact and showed resistance to an initial Cr(VI) concentration of 40 mg L^{-1}. The bacterial growth was slightly affected when the pH of the growth media was adjusted to pH 8. The cell growth was initially affected. The 88% bioreduction obtained with pH 8 was due to fact that there was a drop in the pH of the media due to the depletion of glucose. This drop in pH favored the growth of the bacteria and bioreduction of Cr(VI).

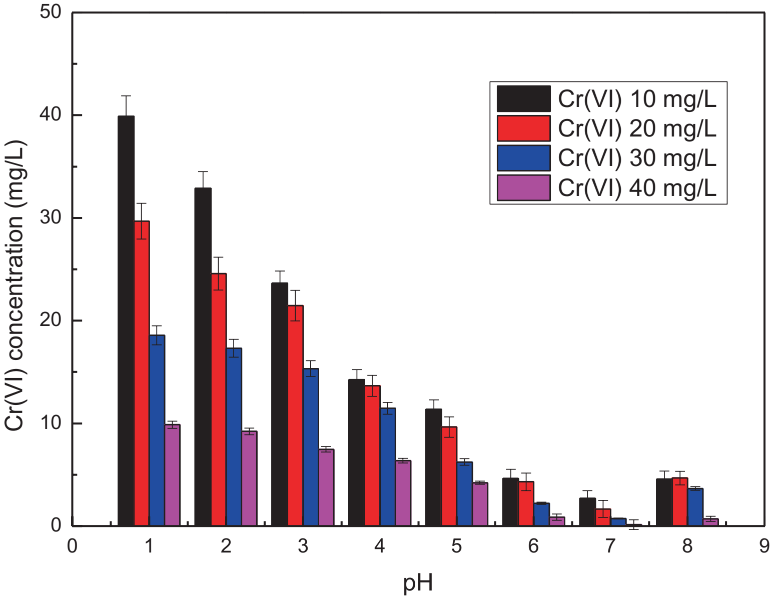


Fig. 13.4 Effect of pH on bioreduction of chromium

13.3.5 Effect of Time on Cr(VI) Reduction

The simultaneous production of Cr(III) and Cr(VI) reduction by *bacterial strains* was reported (Fig. 13.5). It was observed that the concentration of Cr(VI) dropped from an initial concentration of 40 mg L^{-1} to 2.68 mg L^{-1} during the time period studied. The concentration of Cr(III) increased with time. The maximum amount of Cr(III) produced was found to be 37.32 mg L^{-1}. The maximum reduction of Cr(VI) was obtained at 48 h. Figure 13.5 clearly indicated that the Cr(VI) reduction was a time-dependent process. There was a gradual increase in the concentration of the Cr(III) up to 33 h for an initial Cr(VI) concentration of 40 mg L^{-1}, and thereafter, it was observed to be constant.

13.3.6 Specific Cr(VI) Reduction Rate

The specific Cr(VI) reduction rate increases with the initial Cr(VI) concentration. High initial Cr(VI) concentration of 400 mg/l, reported a higher specific reduction rate (0.06 mg/mg cell h). This can be due to the fact that the enriched microbial consortium survived and utilized Cr(VI) concentration in the range of 400 mg/l resisting the antagonistic effect. The enriched microbes reduced Cr(VI) to higher concentrations after 24 days' time. The cell yield decreased at higher loads of Cr(VI) concentrations; this was due to the inhibition effect of Cr(VI) (Figs. 13.6 and 13.7).

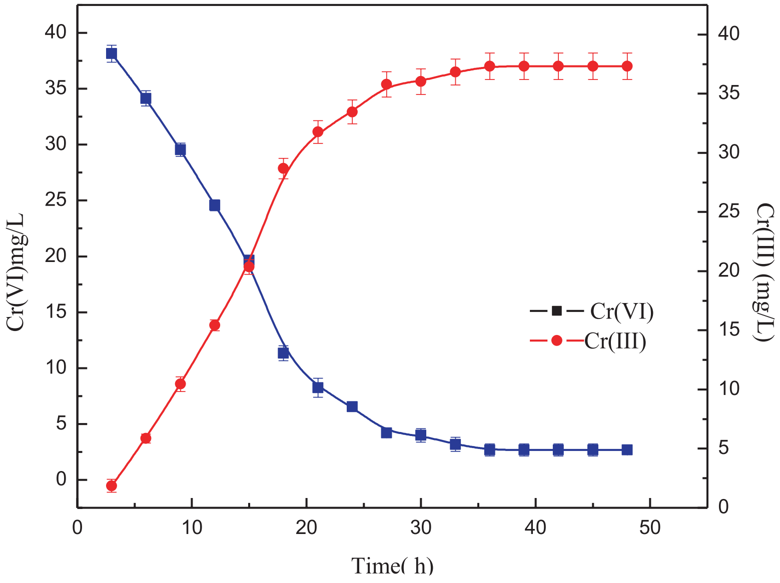


Fig. 13.5 Cr(VI) reduction profile

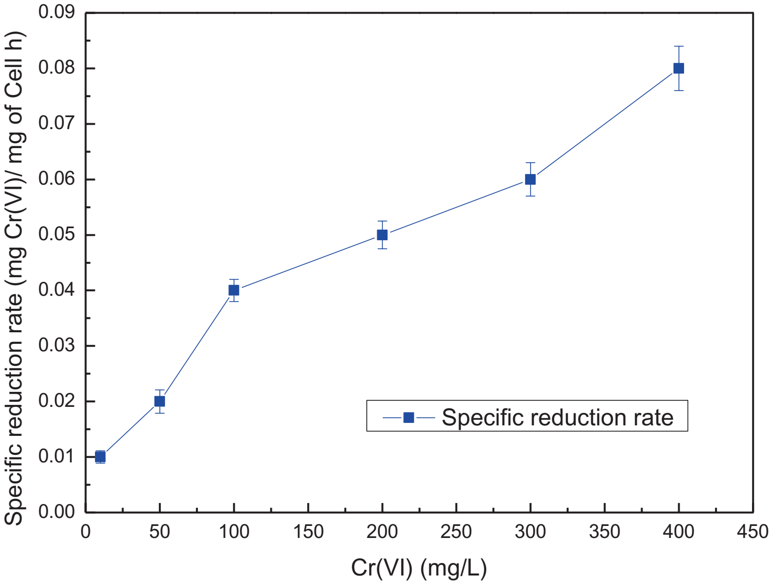


Fig. 13.6 Specific reduction rate

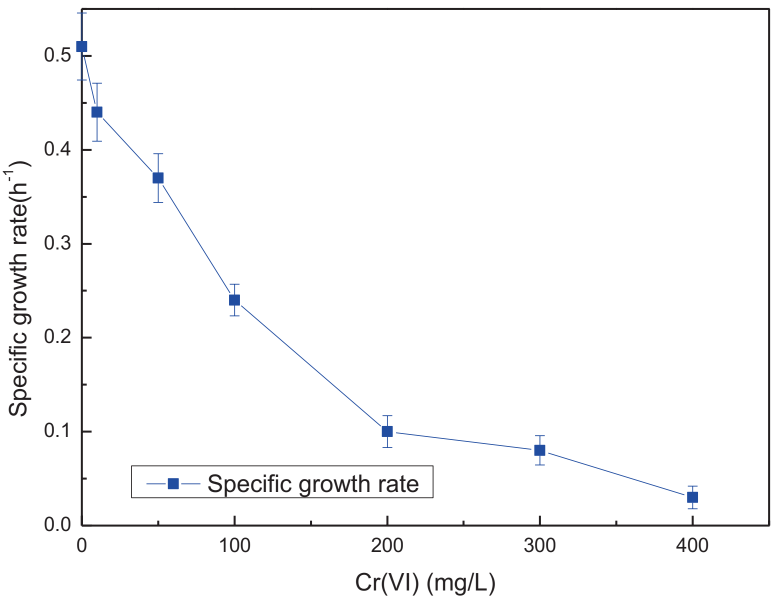


Fig. 13.7 Specific growth rate

13.4 Conclusions

The enriched bacterial culture isolated from hexavalent chromium-contaminated site reduced Cr(VI) at 400 mgL^{-1}. Batch was carried out to study the reduction Cr(VI) with molasses as a carbon source for the growth of enriched culture. The optimum concentration of bacteria and molasses for the reduction of Cr(VI) to Cr(III) was observed as 15 and 34 mg/g of soil, respectively. Ninety-seven percent bioreduction of Cr(VI) was achieved on a 20-day span under the optimum concentration of molasses and bacteria. The reduction of Cr(VI) to Cr(III) is a microbial viable process and results in reduced sludge formation. A maximum specific growth rate of 0.5 h^{-1} was reported at 100 mg L^{-1} of Cr(VI). The bioreduction was significant at near acidic pH.

References

APHA, AWWA (1994) Standard methods for the examination of water and wastewater, 19th edn. American Public Health Association, Washington, DC

Bailey JE, Ollis DF (1986) Biochemical engineering fundamentals, 2nd edn. Tata McGraw Hill, New York

Bopp LH, Elrich HL (1988) Chromate resistance and reduction in Pseudomonas fluorescens strain LB 300. Arch Microbiol 150:426–431

Chen JM, Hao OJ (1997) Biological removal of aqueous hexavalent chromium. J Chem Technol Biotechnol 69:70–76

Cronje KJ, Chetty K, Carsky M, Sahu JN, Meikap BC (2011) Optimization of chromium(VI) sorption potential using developed activated carbon from sugarcane bagasse with chemical activation by zinc chloride. Desal 275:276–284

Eckenfedler WW Jr (1989) Industrial water pollution control. MCGraw Hill Book Company, New York

Liu YG, Xu WH, Zeng GM, Li X, Gao H (2006) Cr(VI) reduction by Bacillus sp isolated from chromium landfill. Process Biochem 41:1981–1986

Liu G, Yang H, Wang J, Jin R, Zhou J, Lv H (2010) Enhanced chromate reduction by resting Escherichia coli cells in the presence of quinine redox mediators. Bioresour Technol 101:8127–8131

Philip L, Iyengar L, Venkobachar C (1998) Cr(VI) reduction by Bacillus coagulans isolated from contaminated soils. J Environ Eng 124:1165–1170

Shen H, Wang YT (1992) Biological reduction of chromium by E. coli. J Environ Eng 120:560–572

Viamjala S, Peyton BM, Petersen JN (2003) Modeling chromate reduction in Shewanella oneidensis MR-1: development of a novel dual-enzyme kinetic model. Biotechnol Bioeng 83:790–797

Wang YT, Shen H (1997) Modelling Cr(VI) reduction by pure bacterial cultures. Water Res 31:727–732

Xu L, Luo M, Li W, wei X, Xie K, Liu L, Jiang C, Liu H (2011) Reduction of hexavalent chromium by Pannonibacter phragmiteus LSSE-09 stimulated with external electron donors under alkaline conditions. J Hazard Mater 185:1169–1176

14

Electrobioremediation of Contaminants: Concepts, Mechanisms, Applications and Challenges

Gaurav Saxena, Indu Shekhar Thakur, Vineet Kumar,
and Maulin P. Shah

Abstract

Environmental pollution has become a serious concern in the current world, and therefore, its mitigation is urgent to safeguard the environment and public health. Bioremediation is identified as an eco-friendly and sustainable remediation technology to minimize and control environmental pollution. It uses an array of microbes/plants to degrade and detoxify environmental contaminants from contaminated matrix for environmental safety. However, its applicability gets limited by several drawbacks: the bioavailability of contaminants and its bioavailability to microbes, quick adaptation of the indigenous microorganisms for biodegradation of a particular contaminant and mass transfer of electron

---

G. Saxena (✉)
Environmental Microbiology and Biotechnology Laboratory, School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, India

Department of Environmental Microbiology (DEM), Babasaheb Bhimrao Ambedkar (Central) University, Lucknow, Uttar Pradesh, India

Laboratory of Microbiology, Department of Microbiology, School of Life and Allied Sciences (SLAS), Baba Farid Institute of Technology, Dehradun, Uttarkhand, India

I. S. Thakur
Environmental Microbiology and Biotechnology Laboratory, School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, India

V. Kumar
Environmental Microbiology and Biotechnology Laboratory, School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, India

Department of Environmental Microbiology (DEM), Babasaheb Bhimrao Ambedkar (Central) University, Lucknow, Uttar Pradesh, India

M. P. Shah
Industrial Waste Water Research Laboratory, Division of Applied and Environmental Microbiology, Enviro Technology Limited, Ankleshwar, Gujarat, India

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_14

acceptors and nutrients to microorganisms responsible for biodegradation. These limitations can be overcome by coupling bioremediation with electrokinetics (EK), i.e. electrobioremediation technology where direct current is applied within subsurface porous media to induce specific transport phenomena. Electrobioremediation involves electrokinetic phenomena for the acceleration and orientation of transport of environmental pollutants and microbes for pollutant bioremediation. It has been identified as an emerging bioremediation technology; however, its applicability to contaminated sites is currently being under investigation. This chapter focuses on the general introduction and mechanism of electrobioremediation technology, electrobioremediation of contaminants, advantages and disadvantages and future prospects and challenges.

Keywords

Electrokinetics · Electrobioremediation · Organic contaminants · Inorganic contaminants · Environmental safety

14.1 Introduction

Land contaminated by anthropogenic activities is of global concern, and where exposure to harmful substances occurs, there is potential for unacceptable risks to human and environmental health. Bioremediation is a well-established technology used to treat biodegradable contaminants, according to concepts based in general on ex situ treatment of excavated material (mainly used in pollutant source removal) and in situ treatment of sites with restricted access (where less disturbance is desirable and extended remediation timescales are acceptable) (Bharagava et al. 2017a, b, c; Bharagava and Saxena 2019a, b; Bharagava et al. 2019). Bioremediation requires environmental conditions which are favourable for the particular biochemical process and interaction between microorganisms, contaminants, nutrients and electron acceptors/donors (Sturman et al. 1995). In situ biodegradation can be limited by contaminant bioavailability, the immediate contact between microorganisms and substances required for contaminant biodegradation, and bioaccessibility, the fraction of these components accessible to microorganisms in the environment (Semple et al. 2004). Consequently, biodegradation processes may occur in the subsurface environment, but not at a rate to mitigate risks at a particular site.

The factors which limit the performance of in situ bioremediation are often highly site-specific and commonly include (1) mass transfer of electron acceptors and nutrients to microorganisms responsible for biodegradation (Simoni et al. 2001), (2) limited bioaccessibility of contaminants (e.g. partitioning to aquifer material) for biodegradation and (3) adaptation of the indigenous microorganisms for biodegradation of a particular contaminant (Mrozik and Piotrowska-Seget 2010). These limitations can be overcome by coupling bioremediation with electrokinetics (EK), a remediation technology where direct current is applied within subsurface porous media to induce specific transport phenomena, namely, (1) electroosmosis, the bulk movement of fluid through pores; (2) electromigration, the movement of ions in solution; and (3) electrophoresis, the movement of charged, dissolved or suspended particles in pore fluid. It is also characterized by the electrolysis of water at the electrodes (Virkutyte et al. 2002). This chapter focuses on the general introduction and mechanism of electrobioremediation of contaminants, advantages and disadvantages and future challenges.

14.2 Electrobioremediation: Concept and General Mechanisms

It is becoming an increasingly popular hybrid technology that uses the combination of bioremediation and electrokinetics for the treatment of environmental pollutants (Maszenan et al. 2011). It involves electrokinetic phenomena for the acceleration and orientation of transport of environmental pollutants and microbes for pollutant bioremediation (Maszenan et al. 2011). Electrokinetics involves the use of several phenomena like diffusion, electrolysis, electroosmosis, electrophoresis and electromigration and uses weak electric currents of about 0.2–2 V cm^{-1} (Saichek and Reddy 2005; Maszenan et al. 2011). A number of studies are available on the use of electrobioremediation technology for contaminated soils (Wick et al. 2007; Yan and Reible 2015). In addition, the applications, potentials and limitations of electrobioremediation technology have been reviewed by many authors (Wick et al. 2007; Maszenan et al. 2011; Gill et al. 2014).

The processes and mechanisms that constitute electrobioremediation include electro-bioattenuation, electro-biostimulation, electro-bioaugmentation, and electro-phytoremediation. Each may be limited by contaminant-microbe-EA/ED contact and mixing or hydraulic transport issues. EK can be used to develop alternative flow fields to increase contact between microorganisms and contaminants or deliver a required amendment to a specific zone that is limited under ambient conditions.

14.2.1 Electro-bioattenuation

Bioattenuation is a low-impact and cost-effective remediation technique but is limited to sites where the contaminant is biodegradable and there is adequate mixing of contaminants, electron acceptors and microorganisms for biodegradation to occur at a suitable rate (Rivett and Thornton 2008). Natural mixing can be enhanced with EK and optimized by increasing the number of electrodes, reversing the electrode polarity, placing electrodes in a radial configuration and rotating the polarity (Luo et al. 2005; Yuan et al. 2013). This is in order to (1) increase the diversity and connectivity of flow paths for potential contact and mixing between microorganisms and contaminants, (2) maintain more uniform pH and moisture conditions as well as microorganism distribution (Huang et al. 2013) and (3) increase the area over which the electric field and enhanced biodegradation is effective. An important control on biodegradation under EK is the voltage gradient that limits the migration rate of substances in situ. This gradient can vary spatially and temporally and when highest maximizes contact between substances and therefore enhances biodegradation.

However, this spatial and temporal variability can lead to uneven biodegradation of contaminants within the matrix.

14.2.2 Electro-biostimulation

EK can enhance the delivery of nutrients (e.g. phosphate), electron acceptors (e.g. nitrate and sulphate (Lohner et al. 2008)) and electron donors (e.g. lactate (Wu et al. 2007)) through different materials at rates greater than diffusion. EK biostimulation in soils has been demonstrated for PCE (Mao et al. 2012), toluene (Tiehm et al. 2010), diesel (Pazos et al. 2012) and PAHs (Xu et al. 2010). In addition to chemical amendments, the gaseous products of water electrolysis (H_2 and O_2) can be used to stimulate reductive dechlorination of PCE and oxidation of VC, respectively (Lohner and Tiehm 2009). This process has been demonstrated in a sequential column experiment where contaminated groundwater was first reduced as it passed through the cathode and then oxidized in the anode column. Biostimulation can also be achieved through the addition of solubilizing agents, to increase the dissolution and bioavailability of hydrophobic contaminants into the aqueous phase (Mulligan 2005). EK phenomena enhance contact between surfactants and bound contaminants at a micro-scale and can deliver surfactants to polluted zones at a plume scale (Saichek and Reddy 2005). These modifications have been demonstrated with synthetic surfactants (Saichek and Reddy 2003), biosurfactants, co-solvents and cyclodextrin (Ko et al. 2000).

14.2.3 Electro-bioaugmentation

EK can enhance the migration of microorganisms through low-permeability soils (Wick et al. 2004; Mao et al. 2012; Mena et al. 2012), despite potential occlusion of cells due to small pore throat size in finely grained materials (DeFlaun and Condee 1997). This enhancement has been attributed to movement of microorganisms preferentially along a flow path through macro-pores within the soil by electroosmotic flow (Wick et al. 2004). EK bioaugmentation has been used within sequential treatment of contaminated soil conditioned with an active degrader species. Mao et al. (2012) used EK to firstly distribute lactate and then the dechlorinating strain *Dehalococcoides* for the treatment of PCE-contaminated soil. EK bioaugmentation can also be effective at redistributing bacteria as a pre-treatment step for soils contaminated with heavy metals (Lee and Kim 2010). Microbes maintain their membrane integrity (Shi et al. 2007) and functionality during transport by EK, and effective biodegradation during migration has been observed for both dextrose (Maillacheruvu and Chinchoud 2011) and diesel (Lee and Lee 2001). Microbes have a strong tendency to attach to sediment and organic matter particles disrupting transport (Mrozik and Piotrowska-Seget 2010), but this can be reduced when using EK by adding surfactants (Wick et al. 2004). It is often difficult to maintain the survival of exogenous microbes introduced to a foreign environment (Megharaj et al. 2011). A possible alternative could be the addition of endospores instead of active bacteria. Endospores are more robust and migrate faster under EK than bacteria due to a highly associated surface charge (Da Rocha et al. 2009).

14.2.4 Electro-phytoremediation

Phytoremediation of recalcitrant organic contaminants in the shallow subsurface (soil and root zone) requires a symbiotic relationship between the plant and the soil microbial community (Teng et al. 2011). Most EK phytoremediation studies focus on the treatment of heavy metal-polluted soils (Cameselle et al. 2013) where the electric field accumulates contaminants around the plant roots increasing bioavailability (Cang et al. 2011). At present, there are no reported studies coupling EK and phytoremediation of organic contaminants; however, EK processes have not been shown to significantly hinder the mechanisms by which plants enhance their degradation. For example, (1) under EK the biomass of certain plant species (lettuce and ryegrass) has been increased under AC electric fields, demonstrating plant health can be maintained (Bi et al. 2010, 2011), and (2) the respiration and biomass of the microbial community can be enhanced under EK phytoremediation (Cang et al. 2012). Therefore, further research should focus on using EK in combination with phytoremediation to treat organic contaminants.

14.3 Applications of Electrobioremediation in Environmental Management

14.3.1 Electrobioremediation of Oil Spills and Petroleum Hydrocarbons

The contamination of our natural environment with oil spills due to petroleum substances and petrochemical compounds has become a serious concern because of their high toxicity and persistence. To date, several remediation approaches have been developed using both physicochemical and biological methods alone or in combination to manage the petroleum contamination. Among them, bioremediation is the most useful technique that accelerates the inherent metabolic activities of the microbes by providing nutrients, electrons donors or acceptors and thus enhances the oxidation and reduction of pollutants. However, the controlling of supply of electron donors or acceptors is the major issue in bioremediation. In contrast to that, electrobioremediation has emerged as a sustainable remediation solution because it use electric current as either an electron donor or an acceptor for oil spill bioremediation (Table 14.1).

There are many reports available in the public domain on the electrobioremediation of oil spills. Toluene is the easiest degradable component of BTEX (benzene, toluene, ethylbenzene and xylenes) compounds, and its degradation has been studied at a variety of anode potentials, both with pure cultures and consortia (Daghio

Table 14.1 Electrokinetic processes for the in situ electrobioremediation of environmental contaminants

Electrokinetic processes	Definition
Electrokinetic bioattenuation	It is an electrokinetic transport process that increases the bioavailability of environmental contaminants and naturally occurring nutrients and electron acceptors limited due to in situ hydrodynamic dispersion
Electrokinetic biostimulation	It is an electrokinetic transport process that allows the addition and delivery of nutrients, electron acceptors and surfactants into contaminated zones regardless of their permeability to increase bioavailability of substances limited due to hydraulic delivery and low-permeability zones
Electrokinetic bioaugmentation	It is an electrokinetic transport of bacterial population to specific zones regardless of their permeability where indigenous community is not adapted
Electrokinetic phytoremediation	It is an electrokinetic transport processes that increase the bioavailability of contaminants

Adapted from Gill et al. (2014)

et al. 2016; Friman et al. 2012; Lin et al. 2014; Zhang et al. 2010). Benzene was degraded in the anode of a BES by mixed cultures enriched from contaminated sediments (Zhang et al. 2010), groundwater (Rakoczy et al. 2013; Wei et al. 2015), wastewater (Wu et al. 2013) and anaerobic sludge (Adelaja et al. 2015). Polycyclic aromatic hydrocarbon (PAH) degradation has also been reported in several studies (Adelaja et al. 2015, 2014; Yan et al. 2012; Zhang et al. 2010). Phenol has been bioelectrochemically degraded by both mixed cultures and a pure culture of *Cupriavidus basilensis* (Friman et al. 2013; Huang et al. 2011). The total petroleum hydrocarbon (TPH) degradation has been extensively assessed in different studies (Chandrasekhar and Venkata Mohan 2012; Cruz Viggi et al. 2015; Li and Yu 2015, Li et al. 2014, Lu et al. 2014a, b; Morris and Jin 2012; Mohan and Chandrasekhar 2011; Wang et al. 2011; Zhang et al. 2015). The oxidation of halogenated hydrocarbons has also been investigated, and bioelectrochemical oxidation of 1,2-dichloroethane (1,2-DCA) with different microbial inocula has been shown to be an attractive technology for the bioremediation of chlorinated compounds (Pham et al. 2009).

Microbial communities play a major role in the electrobioremediation of oil spills and petroleum hydrocarbons. The degradation of phenanthrene by *Shewanella oneidensis* MR1 14,063 in a microbial fuel cell (MFC) was reported (Adelaja et al. 2014). *Pseudomonas aeruginosa* NCTC 10662 has been shown to degrade phenanthrene faster (54.7 $\mu M\ d^{-1}$) than *Shewanella oneidensis* (25.2 $\mu M\ d^{-1}$) under similar operational conditions in an MFC (Adelaja et al. 2014). Morris and colleagues (2009) found that NO3-reducing bacteria dominated the anodic community in a single-chamber MFC in which diesel was degraded with simultaneous current production (Morris et al. 2009). Microbial communities dominated by microorganisms belonging to *Chloroflexi* and to *Nitrospira* were described during PAH degradation (Yan et al. 2012). A recent detailed analysis performed after remediation of TPH-contaminated soil with a BES highlighted that *Proteobacteria* (especially

Betaproteobacteria and *Gammaproteobacteria*) was the most abundant phylum after the treatment (Lu et al. 2014a). The most extensively tested microorganisms in dechlorinating BES belong to the genus *Dehalococcoides*. To date, *Dehalococcoides* spp. are the only known microorganisms able to completely dechlorinate TCE to ethene (Maymó-Gatell et al. 2001; West et al. 2008). Furthermore, a broad survey of microbial community data from a range of oil and hydrocarbon-impacted anoxic environments demonstrated that *Firmicutes* were the most commonly detected followed by the *Gammaproteobacteria*, *Deltaproteobacteria* and *Epsilonproteobacteria* (Gray et al. 2010). Overall, the potential of electrobioremediation technology for the bioremediation of a variety of hydrocarbons, both halogenated and nonhalogenated compounds, is revealed by several studies. The main issue to be faced in the near future will be the scale-up of this technology from lab-scale reactors to field-scale systems that requires further studies.

14.3.2 Electrobioremediation of Industrial Effluents

Electrobioremediation is an emerging hybrid remediation technology coupling bioremediation to electrokinetics. It involves both the advance oxidation process and biological treatment process and is the best solution to achieve the regulatory standard for industrial effluent discharge. There are a very few reports available in the public domain on the electrobioremediation of industrial effluents. Kanagasabi et al. (2012) reported the electrobioremediation of tannery wastewater (TWW) that involved an electrooxidation reactor connected to a column packed with immobilized bacterial biomass. They reported that the electrooxidation was found to obtain maximum COD reduction up to 73.1% at 1.5 A dm^{-2} using raw TWW, and *Bacillus* strain B proved to be superior in terms of COD reduction up to 91.5% with diluted TWW. However, the intimate coupling of electro- and biooxidation recorded good degradation for both raw and diluted TWW samples and achieved 66.2% and 76.6% COD degradation, respectively.

According to Barba et al. (2019), the in situ electrobioremediation (EBR) of clay soil polluted with 2,4-dichlorophenoxyacetic acid (2,4-D) in a two-stage method. First, a fixed-bed biofilm reactor able to biodegrade 2,4-D in wastewater was developed; second, a portion of the biofilm-covered bed was included in the polluted soil and used as a biological permeable reactive barrier (BioPRB), whereas electrokinetics were used to promote the contact between pollutants and microorganisms into the soil. The fixed-bed biofilm reactor successfully treated wastewater polluted with 2,4-D concentrations up to 1200 mg L^{-1} and under nonoxygenated conditions because of the culture ability to use nitrate as an electron acceptor. A portion of the stationary biofilm was later used as a BioPRB in the polluted soil to perform in situ EBR study. The study was performed in a bench-scale set-up using potentiostatic conditions (1.0 V cm^{-1}), room temperature and periodic polarity reversal (2 d^{-1}) in a 10-day batch experiment. The feasibility of the proposed technology was checked by the comparison with a conventional in situ bioremediation test without electrokinetics. The EBR treatment, coupling electrokinetics with the previously developed

BioPRB, offered 85% removal efficiency of 2,4-D after 10 days. According to the low removal efficiency observed in the reference test, it was proved that the electrokinetic transport phenomena improved contact between pollutants and microorganisms and clearly increased 2,4-D removal rate.

14.3.3 Electrobioremediation of Contaminated Soil

One of the major challenges in environmental biotechnology is the improvement of in situ soil decontamination efficiency. Several studies are available in the public domain on the electrobioremediation of pollutant-contaminated soil.

According to Barba et al. (2019), a microbial culture that can biodegrade oxyfluorfen was grown as a biofilm in a fixed-bed biofilm reactor. The biofilm reactor was operated under stationary conditions and can degrade 200 mg L^{-1} of oxyfluorfen in approximately 30 h. The culture uses both oxygen and nitrate as electron acceptors and can degrade oxyfluorfen concentrations up to 800 mg L^{-1}. A portion of the biofilm reactor was used as a central permeable biological barrier for the in situ EBR of oxyfluorfen-polluted clay soil. The microbial activity was detected in the soil after a 2-week batch period probably because of the biofilm detachment and microbial EK transport. The reference tests prove that the combination of the biological and EK mechanisms is necessary. This technology can be used as a bioaugmentation method for the EBR technology, although the low removal efficiency suggests that oxyfluorfen has low mobility, and higher retention time is necessary to obtain successful results.

According to Azhar et al. (2016), they investigate the effectiveness of *Pseudomonas putida* bacteria as a biodegradation agent to remediate contaminated soil. 5 kg of kaolin soil was spiked with 5 g of zinc oxide. During this process, the anode reservoir was filled with *Pseudomonas putida*, while the cathode was filled with distilled water for 5 days at 50 V of electrical gradient. The X-ray fluorescence (XRF) test indicated that there was a significant reduction of zinc concentration for the soil near the anode with 89% removal. The bacteria count is high near the anode which is 1.3 × 107 cfu/gww, whereas the bacteria count at the middle and near the cathode was 5.0 × 106 cfu/gww and 8.0 × 106 cfu/gww, respectively. The migration of ions to the opposite charge of electrodes during the electrokinetic process resulted from the reduction of zinc. The results obtained proved that the electrobioremediation reduced the level of contaminants in the soil sample. Thus, the electrobioremediation technique has the potential to be used in the treatment of contaminated soil.

According to Wang et al. (2015), the highly efficient degradation of *n*-hexadecane in soil is realized by alternating bioremediation and electrokinetic technologies. Using an alternating technology instead of simultaneous application prevented competition between the processes that would lower their efficiency. For the consumption of the soil-dissolved organic matter (DOM) necessary for bioremediation by electrokinetics, bioremediation was performed first. Because of the utilization and loss of the DOM and water-soluble ions by microbial and electrokinetic processes, respectively, both of them were supplemented to provide a basic carbon resource, maintain a high electrical conductivity and produce a uniform distribution of ions. The moisture and bacteria were also supplemented. The optimal DOM supplement (20.5 mg·kg^{-1} glucose; 80–90% of the total natural DOM content in the soil) was calculated to avoid competitive effects (between the DOM and *n*-hexadecane) and to prevent nutritional deficiency. The replenishment of the water-soluble ions maintained their content equal to their initial concentrations. The degradation rate of *n*-hexadecane was only 167.0 mg kg^{-1} d^{-1} (1.9%, w/w) for the first 9 days in the treatments with bioremediation or electrokinetics alone, but this rate was realized throughout the whole process when the two technologies were alternated, with a degradation of 78.5% ± 2.0% for the *n*-hexadecane after 45 days of treatment.

According to Yan and Reible (2015), the purpose of this research was to demonstrate a reactive capping technique, an electrode-enhanced cap, to produce favourable conditions for hydrocarbon degradation and evaluate this reactive capping technique for contaminated sediment remediation. Two graphite electrodes were placed horizontally at different layers in a cap and connected to external power of 2 V. Redox potentials increased and pH decreased around the anode. Phenanthrene concentration decreased and PAH degradation genes increased in the vicinity of the anode. Phenanthrene concentrations at 0–1 cm sediment beneath the anode decreased to ~50% of initial concentration over ~70 days, while phenanthrene levels in control reactor kept unchanged. A degradation model of electrode-enhanced capping was developed to simulate reaction-diffusion processes, and model results show that a reaction-dominated region was created in the vicinity of the anode. Although the degradation-dominated region was thin, transport processes in a sediment cap environment are typically sufficiently slow to allow this layer to serve as a permeable reactive barrier for hydrocarbon decontamination.

According to Shi et al. (2007), they represented data about the influence of direct current (DC) on the membrane integrity, adenosine triphosphate (ATP) pools, physicochemical cell surface properties, degradation kinetics and culturability of fluorene-degrading *Sphingomonas* sp. LB126. Flow cytometry was applied to quantify the uptake of propidium iodide (PI) and the membrane potential-related fluorescence intensities (MPRFI) of individual cells within a population. Adenosine tri-phosphate contents and fluorene biodegradation rates of bulk cultures were determined and expressed on a per cell basis. The cells' surface hydrophobicity and electric charge were assessed by contact angle and zeta potential measurements, respectively. Relative to the control, DC-exposed cells exhibited up to 60% elevated intracellular ATP levels and yet remained unaffected on all other levels of cellular integrity and functionality tested. Our data suggest that direct current ($X = 1$ V cm^{-1}; $J = 10.2$ mA cm^{-2}) as typically used for electrobioremediation measures has no negative effect on the activity of the polycyclic aromatic hydrocarbon (PAH)-degrading soil microorganism, thereby filling a serious gap of the current knowledge of the electrobioremediation methodology.

14.3.4 Electrobioremediation of Heavy Metals

Bioremediation is the use of living organism's whether microbes and plants to degrade and detoxify the environmental contaminants (Chandra et al. 2015; Saxena and Bharagava 2016; Saxena and Bharagava 2017; Saxena and Bharagava 2019). However, combining phytoremediation with electrokinetic remediation could be an excellent strategy to enhance metal mobility in contaminated soil and facilitate their plant uptake and thus phytoremediation (Saxena et al. 2019a, b). Most EK phytoremediation studies focus on the treatment of heavy metal-polluted soils (Cameselle et al. 2013) where the electric field accumulates contaminants around the plant roots, increasing bioavailability (Cang et al. 2011). For instance, Mao et al. (2016) evaluated the feasibility of electrokinetic remediation coupled with phytoremediation to remove Pb, As and Cs from contaminated paddy soil. Results revealed that the solubility and bioavailability of Cs and As were significantly increased by the electrokinetic field (EKF) and thereby lower the pH of contaminated soil. Furthermore, they observed that EKF significantly enhanced the bioaccumulation of As and Cs in plant roots and shoots and thus enhanced phytoremediation efficiency. However, the optimization of electrical parameters such as electrical field intensity, current application mode, distance between the electrodes, stimulation period and their effect on the mobility and bioavailability of HMs are the associated key challenges (Mao et al. 2016). Further, the application of electrokinetic phytoremediation for the organic contaminants and mixed contaminants (organic and inorganic) has not also been reported so far. Therefore, further research should focus on using EK in combination with phytoremediation to treat organic contaminants.

14.4 Factors Affecting Electrobioremediation

The principal environmental properties that influence EK-BIO are the electrolyte (i.e. groundwater chemistry or soil moisture) through which the current travels, the geological strata that influence EK phenomena, hydrodynamics that introduce advection as an additional transport vector, physical heterogeneity that can alter transport rates and the mixed nature of contaminants found at many sites. The choice of an appropriate anodic material affects the selectivity and efficiency of the hydrocarbon removal process (Anglada et al. 2009). The electrode material should comply with the following properties: (i) high physical and chemical stability, (ii) high electrical conductivity, (iii) catalytic activity and selectivity for the target compounds and (iv) low cost/life ratio. Inexpensive and long life service materials should be favoured for the oxidation of hydrocarbons. For stimulation of microbial metabolism with anodes serving as electron acceptors, stainless steel electrodes (Morris et al. 2009; Morris and Jin 2012, 2008; Yan et al. 2012) or conductive carbon and graphite have been used (Table 14.2). A comparison of anodic materials used in different studies, in terms of removal efficiencies, is difficult, because factors other than the electrode material may affect the degradation rate. The anode in a BES is the final electron acceptor in microbial metabolism. The energy gain for

Table 14.2 Some studies on the electrobioremediation of environmental contaminants

Reference	Microbes/mixed culture/ consortium	Treated medium	Redox mediator	Electrode material	Electrode potential	Maximum voltage	Contaminant	Removal efficiency
Zhang et al. (2010)	Mixed culture	Sediment-seawater Slurry (1:4)	ND	Unpolished Graphite rod	+ 500 mV	NA	Naphthalene	~ 100% removal within 9 days from 100 μM
Morris and Jin (2008)	Consortium dominated by NO_3^--reducing bacteria (i.e. *Citrobacter* sp., *Pseudomonas* sp. and *Stenotrophomonas* sp.)	Refinery Wastewater and mineral medium (50:50)	ND	Stainless steel Scrubber	NA	120 mW m^{-2} of cathode	Diesel	NA
Daghio et al. (2016)	Mixed culture dominated by $SO4^{2-}$ reducers (i.e. *Desulfobulbaceae* and *Desulfobacteraceae*)	Artificial Sea water	ND	Graphite plate	+ 200 mV	301 mA m^{-2}	Toluene	~ 1 mg L^{-1} d^{-1}
Cruz Viggi et al. (2015)	Consortium dominated by α-*Proteobacteria*, γ-*Proteobacteria* and δ-*Proteobacteria*	Marine sediment	ND	Graphite rod	NA	NA	TPH	21 ± 1% removal within 200 days from 11.9 ± 0.12 gkg^{-1}
Yan et al. (2012)	Mixed culture dominated by *Nitrospira* sp. and *Chloroflexi*	Freshwater Sediment	ND	Stainless steel (mesh)	NA	17.1 ± 3.8 mV (average over 240 days)	Phenanthrene	0.0836 d^{-1} (0–22 days) with The addition of FeOOH
Yan et al. (2012)	Mixed culture dominated By *Nitrospira* sp. and *Chloroflexi*	Freshwater Sediment	ND	Stainless steel (mesh)	NA	17.1 ± 3.8 mV (average over 240 Days)	Pyrene	0.1363 d^{-1} (0–22 days) with The addition of FeOOH
Friman et al. (2013)	*Cupriavidus basilensis*	Mineral medium	Self-produced Mediator (+140 mV Vs SHE)	Graphite rod	+ 325 mV	478 mA m^{-2}	Phenol	0.36 mg L^{-1} h^{-1}

(continued)

Table 14.2 (continued)

Reference	Microbes/mixed culture/ consortium	Treated medium	Redox mediator	Electrode material	Electrode potential	Maximum voltage	Contaminant	Removal efficiency
Rakoczy et al. (2013)	*Consortium* dominated by δ-*Proteobacteria* (i.e. *Desulfobacteraceae*, *Desulfobulbaceae* and *Geobacteraceae*)	Benzene- and sulphide-contaminated groundwater	ND	Graphite fibres	NA	550 μA	Benzene	18–80% removal from 150–250 μM
Venkidusamy et al. (2016)	Mixed culture rich in γ-*Proteobacteria*	Mineral medium	ND	Carbon fibre brush	NA	114.54 mA m^{-2}	Diesel	93.5 ± 0.6% removal from 8000 mg L^{-1} within 30 days
Zhang et al. (2010)	*Geobacter metallireducens*	Mineral medium	ND	Unpolished graphite rod	+ 500 mV	1 mA	Toluene	NA
Lu et al. (2014a)	Mixed culture dominated by β-*Proteobacteria* (e.g. *Bordetella* sp.) and γ-*Proteobacteria* (e.g. *Pseudomonas*)	Contaminated soil	ND	Carbon cloth	NA	73.0 ± 0.1 mA	TPH	73.1% removal within 64 days from 11.46 g kg^{-1}
Adelaja et al. (2014)	Pseudomonas aeruginosa	Mineral medium	ND	Carbon felt	NA	0.19 ± 0.05 mW m^{-2}	Phenanthrene	54.70 ± 0.60 μM d^{-1}
Friman et al. (2012)	*Pseudomonas putida* F1	*Pseudomonas putida* F1	ND	Graphite rod	+ 325 mV	23 mA m^{-2}	Toluene	80% removal within 147 hours after five additions (100 mg L^{-1} each)
Lu et al. (2014b)	Mixed culture dominated by β-*Proteobacteria* (e.g. *Comamonas* sp.) and γ-*Proteobacteria* (e.g. *Pseudomonas*	Contaminated soil	ND	Biochar	NA	85.9 ± 0.1 mA m^{-2}	TPH	78.7% removal within 64 days from 11.46 g kg^{-1}

Adelaja et al. (2014)	*Shewanella oneidensis*	Mineral medium	ND	Carbon felt	NA	0.51 ± 0.03 mW m^{-2}	Phenanthrene	25.20 ± 5.15 μM d^{-1}
Azhar et al. (2016)	*Pseudomonas putida*	Contaminated soil	ND	Unknown	+ 50 V	NA	HMs	See paper
Barba et al. (2019)	Mixed culture	Contaminated soil	ND	Unknown	1 V cm^{-1}	NA	Oxyfluorfen	15%
Mena et al.	Consortium of diesel oil-degrading microbes	Contaminated soil	ND	Graphite plates	0.5–1.0 V cm^{-1},	NA	Diesel	Variable (see paper)
Yan and Reible (2015)	Consortium of PAH-degrading microbes	Contaminated sediments	ND	Graphite	2 V	22–32 mA/m^2	Phenanthrene	50%
Shi et al. (2007)	*Sphingomonas* sp. LB126	Mineral medium	ND	Titanium-iridium electrodes	1 V cm^{-1}	mA cm^{-2}	Fluorine	NA
Barba et al. (2019)	Consortium of microbes	Polluted wastewater	ND	Unknown	1 V cm^{-1}	NA	2,4-dichlorophenoxyacetic acid	85% within 10 days

ND not detected, *NA* not applicable, *TPH* total petroleum hydrocarbon, *HMs* heavy metals, *PAH* polyaromatic hydrocarbons the microorganisms is higher using electron acceptors with a more positive potential (Madigan et al. 290 2011); thus, it is reasonable to hypothesize that a more positive anodic potential can enhance hydrocarbon oxidation in BES. Redox mediators enable electron transfer to and from an electrode. As artificial mediators can be toxic and inhibitory to microbial activity, mediator-free BES are preferable during bioremediation. Artificial mediators also pose some of the same disadvantages of the soluble electron acceptors, as they could diffuse away from the reaction area and interact with other processes, therefore decreasing the efficiency. The extension of the radius of influence of an electrode is one of the most important aspects to address before applying BES-based technologies for the bioremediation of soil and sediment. The mass transfer of the chemical species (e.g. groundwater flow) could extend the radius of influence of the electrode, particularly if the function of the electrode is to generate a soluble electron donor or acceptor in situ.

Contamination in the natural environment often occurs as mixtures of organic and inorganic contaminants that may require treatment by different remediation technologies. Remediating mixed contaminants with EK-BIO is poorly studied but could involve sequential processes in which inorganic contaminants are first removed by EK followed by EK-BIO treatment for the organic contaminants. Heavy metals can inhibit microbial growth, especially as their extraction using EK requires mobilization into solution, thereby increasing their bioavailability (Cang et al. 2007). The application of EK-BIO determines the electrode material that should be used. Durability is also a factor; metal electrodes corrode more easily especially at low pH (Suni et al. 2007) and should therefore be used with pH control or with an appropriate surface coating to reduce corrosion. However, electrode coatings that raise the surface potential of the electrode will generate more secondary products from electrochemical reactions, such as chlorine (Cl2), hydrogen peroxide (H2O2) or high-energy free radicals (e.g. O2__ or _OH), which inhibit microorganisms adjacent to the electrode (Li et al. 2002; Tiehm et al. 2009). This is important in EK-BIO applications where the electrodes are in close proximity to the degrading microorganisms. Hence, metal electrodes may be most suitable for small-scale application, whereas metal electrodes engineered to resist corrosion are more suitable for large-scale applications where long distances are involved. Titanium and stainless steel are noted as effective electrode materials at the field scale because they are reliable with a low associated economic cost (Virkutyte et al. 2002). Electrodes can be installed in different configurations, for example, unidirectional, bidirectional, radial-pairs or radial-bidirectional. These can be applied to achieve different outcomes. For example, a bidirectional or radial-bidirectional set-up is suitable for the migration of amendment evenly and at high concentration (Wu et al. 2013), whereas a radial-pairs configuration is suitable for mixing substances in situ. Thus, these factors should be considered before applying electrobioremediation to contaminated matrix.

14.5 Field Studies

Despite considerable scientific interest, field-scale bioelectrochemical systems have not yet been tested and verified under fully representative conditions, and concerns have also been raised regarding their actual scalability. Although the scalability of a bioelectrochemical system poses some intrinsic challenges, lessons can be learned from pure electrochemical processes where hundreds of small units provide high production rates and volumes. Indeed, to date a number of consolidated electrochemical remediation technologies are commercially available and widely applied for in situ treatment of a variety of inorganic and organic pollutants (Trombly 2008). These technologies are not typically used for the direct degradation of the contaminants but apply low-voltage direct current, by means of electrode arrays, to favour the electrokinetic movement of pollutants from soils into "treatment zones" where they are removed from the water by adsorption, immobilization or (bio)degradation. Electric current flows between pairs of anodes and cathodes suitably deployed in contaminated subsurface environments (e.g. the vadose zone of an aquifer). In such systems, the applied current density is in the range of a few amperes per square metre ($A\ m^{-2}$), driven by a potential difference that is typically in the order of a few volts per centimetre ($V\ cm^{-1}$). One relevant example is the "Lasagna Process" (Ho et al. 2002), developed by a consortium of industries (DuPont, General Electrics and Monsanto) in collaboration with US federal agencies (EPA, DOE), providing large-scale demonstrations of the feasibility of the technology for in situ treatment of a variety of contaminants, including TCE (Ho et al. 1999a, 1999b).

14.6 Merits and Demerits of Electrobioremediation

One of the main benefits lies in the fact that the conversion of contaminants can be manipulated by altering the potential of the anode or the cathode. The energy levels can be set, thus setting favourable thermodynamic conditions for the reaction and adapting to in situ circumstances. Furthermore, the flux of electrons can be maintained stably for extended time periods. The possibility of a constant electron flow implies that the electrode can serve as a virtually inexhaustible electron acceptor/donor, lowering the operational costs because continuously supplying electron acceptors/donors is not needed (Morris and Jin 2008). Furthermore, since no chemical injection is required, the expenses and need for transport and storage are eliminated (Rabaey and Keller 2008). Overall, this makes the bioelectrochemical approach a cleaner and cheaper process compared to traditional strategies (Aulenta et al. 2009). It is important to note that a complete evaluation of the cost associated to the application of BES for bioremediation is not possible yet due to the lack of experimental data on large-scale plants. Another important advantage of BES-based approaches is the selectivity that can be achieved compared to physicochemical strategies that may lead to the formation of products with greater toxicity than the parent contaminants. In some contaminated sites, biodegradation of pollutants could be limited by the lack of microorganism carrying the required metabolic pathways. In such cases, the addition of selected microbial populations can be a suitable strategy (El Fantroussi and Agathos 2005). Persistence of the inoculated microorganisms however can be limited due to competition with indigenous microbial communities, predation and/or unfavourable environmental conditions (Careghini et al. 2015; Daghio et al. 2015). BES-based approaches may facilitate bioaugmentation by enabling microbial inoculum to persist by using electrodes pre-colonized with acclimated populations (Venkidusamy et al. 2016). In terms of process monitoring, the electric signal generated in a BES may be used as a real-time measurement of the in situ microbial activity in order to gain information about degradation rates (Tront et al. 2008; Williams et al. 2010). The energy harvested could also be used to power other electrical sensors for in situ monitoring (Lovley 2006; Shantaram et al. 2005). The main drawback during the oxidation of hydrocarbons is that aerobic degradation is usually a faster process than biodegradation in the absence of O2, because of the more efficient activation of oxygenases during the first step of the pathway (Weelink et al. 2010). Other issues, such as the choice of appropriate materials and potentials, or the effect of the radius of influence and limitations during scale-up, should not be overlooked during electrobioremediation feasibility studies. A major bottleneck of electrochemical bioremediation of hydrocarbons under anaerobic conditions is initiation of the degradation pathway (Bertrand et al. 2011). In oxygen evolution through water oxidation usually results in a decrease in pH that may impose further effects on biodegradation. Type, design and electrode material are determining factors of oxygen evolution potential and treatment.

14.7 Future Prospects and Challenges

Future research directions should perhaps be directed towards adjustment of physicochemical conditions in situ to promote the activity of organisms involved in the bioelectrochemical removal of contaminants such as adjustment of pH bcause bacterial activity is affected by pH and most microorganisms have an optimum at circum-neutral pH (Alvarez and Illman 2006); however, in contaminated sites acidic or alkaline conditions may occur (Bamforth and Singleton 2005). BES could also be used to change the chemical equilibrium by scavenging metabolites that accumulate during the biodegradation of contaminants and which may inhibit further degradation. An example can be represented by sulphide scavenging as previously reported (Daghio et al. 2016; Dutta et al. 2008; Rakoczy et al. 2013; Zhang et al. 2014). However other mechanisms of metabolite scavenging are worthy of investigation. Recently, it has been reported that bioelectrogenic bacteria on the anodes of sediment MFC can use plant root exudates as substrates leading to several beneficial effects, such as electricity production (Kaku et al. 2008; Schamphelaire et al. 2008) or reduction of greenhouse gas emissions (Arends et al. 2014). The combined treatment with the macrophyte *Acorus calamus* and MFC for the degradation of pyrene and benzo[a]pyrene in contaminated sediments has also been proposed to achieve higher degradation rate (Yan et al. 2015). Another innovative opportunity to use BES for the bioremediation comes from the possibility to drive the production of organic compounds (e.g. acetate) at the cathode (Logan and Rabaey 2012). The main issue to be faced in the near future will be the scale-up of this technology from lab-scale reactors to field-scale systems. This will allow a better comparison of the electrobioremediation strategies with current technologies used for in situ bioremediation.

14.8 Conclusion and Recommendations

The electrobioremediation of oil spills is a rapidly growing field. The potential of this innovative technology for the bioremediation of a variety of hydrocarbons, both halogenated and nonhalogenated compounds, is revealed by several studies. The following conclusions and recommendations can be made from this review:

(a) When EK is applied in the natural environment, complex physicochemical processes generate non-uniform pH, voltage and moisture gradients that can affect bioremediation performance and need to be considered on a site-specific basis, for example, groundwater flow will influence amendment transport and pH changes at the electrodes.
(b) Numerous electrode material and configuration options exist to optimize the EK-BIO treatment.
(c) The investigation of the effectiveness of EK-BIO applied to novel contaminants as well as organic and inorganic contaminant mixtures is required.
(d) Feasibility of electrobioremediation combined with other remediation technologies such as chemical oxidation/reduction and phytoremediation should be tested to achieve better treatment efficiency.
(e) Electrode configurations and treatment optimization to accommodate field-scale complexity and effects of electrokinetics on microbial communities should be evaluated.
(f) Good practice guidelines on EK-BIO implementation at the field scale could be developed to support the application of well-designed and effective EK-BIO treatment, without unintended adverse effects.
(g) Field studies are very scare, and hence, testing at field scale should be required for better cost comparison and applicability to contaminated sites.
(h) Progresses should be made to develop more robust, reliable and advanced field equipment for electrobioremediation purpose.
(i) Environmental impacts of electrobioremediation should also be considered before applying to the field.
(j) Electrobioremediation aims at acting on microbial communities by favouring some functions to the detriment of other functions considered undesirable, and hence, adverse effects of electrokinetics on microbial communities should be studied.

(k) The design and operational conditions must also be optimized to reduce the device internal resistance and improve electrochemical processes.

(l) Design and engineering on the site receiving the bioremediation device are yet to be imagined and will obviously have to be tailored to the specificities of each implementation site (e.g. geomorphology, climate, flow regime, pollutant loads).

References

Adelaja O, Keshavarz T, Kyazze G (2014) Enhanced biodegradation of phenanthrene using different inoculum types in a microbial fuel cell. Eng Life Sci 14:218–228

Adelaja O, Keshavarz T, Kyazze G (2015) The effect of salinity, redox mediators and temperature on anaerobic biodegradation of petroleum hydrocarbons in microbial fuel cells. J Hazard Mater 283:211–217

Alvarez PJJ, Illman WA (2006) Bioremediation and natural attenuation. Wiley

Anglada A, Urtiaga A, Ortiz I (2009) Contributions of electrochemical oxidation to waste-water treatment: fundamentals and review of applications. J Chem Technol Biotechnol 84:1747–1918

Arends JBA, Speeckaert J, Blondeel E, De Vrieze J, Boeckx P, Verstraete W, Rabaey K, Boon N (2014) Greenhouse gas emissions from rice microcosms amended with a plant microbial fuel cell. Appl Microbiol Biotechnol 98(7):3205–3217

Aulenta F, Canosa A, Reale P, Rossetti S, Panero S, Majone M (2009) Microbial reductive dechlorination of trichloroethene to ethene with electrodes serving as electron donors without the external addition of redox mediators. Biotechnol Bioeng 103(1):85–91

Azhar ATS, Nabila ATA, Nurshuhaila MS, Shaylinda MZN, Azim MAM (2016) Electromigration of contaminated soil by electro-bioremediation technique. IOP Conf Ser Mater Sci Eng 136:012023

Bamforth SM, Singleton I (2005) Bioremediation of polycyclic aromatic hydrocarbons: current knowledge and future directions. J Chem Technol Biotechnol 80(7):723–736

Barba S, Carvela M, Villaseñor J, Rodrigo MA, Cañizares P (2019) Fixed-bed biological barrier coupled with electrokinetics for the electrobioremediation of 2,4-dichlorophenoxyacetic acid polluted soil. J Chem Technol Biotechnol 94(8):2684–2692

Bertrand J-C, Caumette P, Lebaron P, Matheron R, Normand P, Sime-Ngando T (2011) Environmental microbiology: fundamentals and applications. Springer, New York

Bharagava RN, Chowdhary P, Saxena G (2017a) Bioremediation: an ecosustainable green technology: its applications and limitations. In: Bharagava RN (ed) Environmental pollutants and their bioremediation approaches, 1st edn. CRC Press/Taylor & Francis Group, Boca Raton, pp 1–22. https://doi.org/10.1201/9781315173351-2

Bharagava RN, Saxena G, Chowdhary P (2017b) Constructed wetlands: an emerging phytotechnology for degradation and detoxification of industrial wastewaters. In: Bharagava RN (ed) Environmental pollutants and their bioremediation approaches, 1st edn. CRC Press/Taylor & Francis Group, Boca Raton, pp 397–426. https://doi.org/10.1201/9781315173351-15

Bharagava RN, Saxena G (2019a) Bioremediation of industrial waste for environmental safety: biological agents and methods for industrial waste management, 1st edn. Springer, Singapore. https://doi.org/10.1007/978-981-13-3426-9

Bharagava RN, Saxena G (2019b) Progresses in bioremediation technologies for industrial waste treatment and management: challenges and future prospects. In: Bharagava RN, Saxena G (eds) Bioremediation of industrial waste for environmental safety: biological agents and methods for industrial waste management, 1st edn. Springer, Singapore. https://doi.org/10.1007/978-981-13-3426-9_21

Bharagava RN, Saxena G, Mulla SI (2019) Introduction to industrial wastes containing organic and inorganic pollutants and bioremediation approaches for environmental management. In: Saxena G, Bharagava RN (eds) Bioremediation of industrial waste for environmental safety: volume i: industrial waste and its management. Springer, Singapore. https://doi.org/10.1007/978-981-13-1891-7_1

Bi R, Schlaak M, Siefert E, Lord R, Connolly H (2010) Alternating current electrical field effects on lettuce (Lactuca sativa) growing in hydroponic culture with and without cadmium contamination. J Appl Electrochem 40(6):1217–1223

Bi R, Schlaak M, Siefert E, Lord R, Connolly H (2011) Influence of electrical fields (AC and DC) on phytoremediation of metal polluted soils with rapeseed (Brassica napus) and tobacco (Nicotiana tabacum). Chemosphere 83(3):318–326

Cameselle C, Chirakkara RA, Reddy KR (2013) Electrokinetic-enhanced phytoremediation of soils: status and opportunities. Chemosphere 93(4):626–636

Cang L, Zhou D-M, Alshawabkeh AN, Chen H-F (2007) Effects of sodium hypochlorite and high pH buffer solution in electrokinetic soil treatment on soil chromium removal and the functional diversity of soil microbial community. J Hazard Mater 142(1-2):111–117

Cang L, Wang Q–Y, Zhou D–M, Xu H (2011) Effects of electrokinetic-assisted phytoremediation of a multiple-metal contaminated soil on soil metal bioavailability and uptake by Indian mustard. Sep Purif Technol 79(2):246–253

Cang L, Zhou D-M, Wang Q-Y, Fan G-P (2012) Impact of electrokinetic-assisted phytoremediation of heavy metal contaminated soil on its physicochemical properties, enzymatic and microbial activities. Electrochim Acta 86:41–48

Careghini A, Saponaro S, Sezenna E, Daghio M, Franzetti A, Gandolfi I, Bestetti G (2015) Lab-scale tests and numerical simulations for in situ treatment of polluted groundwater. J Hazard Mater 287:162–170

Chandra R, Saxena G, Kumar V (2015) Phytoremediation of environmental pollutants: an eco-sustainable green technology to environmental management. In: Chandra R (ed) Advances in biodegradation and bioremediation of industrial waste, 1st edn. CRC Press/Taylor & Francis Group, Boca Raton, pp 1–30. https://doi.org/10.1201/b18218-2

Chandrasekhar K, Venkata Mohan S (2012) Bio-electrochemical remediation of real field petroleum sludge as an electron donor with simultaneous power generation facilitates biotransformation of PAH: effect of substrate concentration. Bioresour Technol 110:517–525

Cruz Viggi C, Presta E, Bellagamba M, Kaciulis S, Balijepalli SK, Zanaroli G, Petrangeli Papini M, Rossetti S, Aulenta F (2015) The “Oil-Spill Snorkel”: an innovative bioelectrochemical approach to accelerate hydrocarbons biodegradation in marine sediments. Front Microbiol 6:881

Da Rocha UN, Tótola MR, Pessoa DMM, Júnior JTA, Neves JCL, Borges AC (2009) Mobilisation of bacteria in a fine-grained residual soil by electrophoresis. J Hazard Mater 161(1):485–491

Daghio M, Tatangelo V, Franzetti A, Gandolfi I, Papacchini M, Careghini A, Sezenna E, Saponaro S, Bestetti G (2015) Hydrocarbon degrading microbial communities in bench scale aerobic biobarriers for gasoline contaminated groundwater treatment. Chemosphere 130:34–39

Daghio M, Vaiopoulou E, Patil SA, Suárez-Suárez A, Head IM, Franzetti A, Rabaey K (2016) Anodes stimulate anaerobic toluene degradation via sulfur cycling in marine sediments. 1033 Appl Environ Microbiol 82:297–307

DeFlaun MF, Condee CW (1997) Electrokinetic transport of bacteria. J Hazard Mater 55(1–3):263–277

Dutta P, Rabaey K, Yuan Z, Keller J (2008) Spontaneous electrochemical removal of aqueous sulfide. Water Res 42(20):4965–4975

El Fantroussi S, Agathos SN (2005) Is bioaugmentation a feasible strategy for pollutant removal and site remediation? Curr Opin Microbiol 8(3):268–275

Friman H, Schechter A, Nitzan Y, Cahan R (2012) Effect of external voltage on Pseudomonas putida F1 in a bio electrochemical cell using toluene as sole carbon and energy source. Microbiology 158:414–423

Friman H, Schechter A, Nitzan Y, Cahan R (2013) Phenol degradation in bio-electrochemical cells. Int Biodeterior Biodegrad 84:155–160

Gill RT, Harbottle MJ, Smith JWN, Thornton SF (2014) Electrokinetic-enhanced bioremediation of organic contaminants: a review of processes and environmental applications. Chemosphere 107:31–42

Gray ND, Sherry A, Hubert C, Dolfing J, Head IM (2010) Methanogenic degradation of petroleum hydrocarbons in subsurface environments. remediation, heavy oil formation, and energy recovery Adv Appl Microbiol 72:137–161

Ho SV, Athmer C, Sheridan PW, Hughes BM, Orth R, McKenzie D, Brodsky PH, Shapiro A, Thornton R, Salvo J, Schultz D, Landis R, Griffith R, Shoemaker S (1999a) The lasagna technology for in situ soil remediation. 1. Small field test. Environ Sci Technol 33:1086–1091

Ho SV, Athmer C, Sheridan PW, Hughes BM, Orth R, McKenzie D, Brodsky PH, Shapiro AM, Sivavec TM, Salvo J, Schultz D, Landis R, Griffith R, Shoemaker S (1999b) The lasagna technology for in situ soil remediation. 2. Large field test. Environ Sci Technol 33:1092–1099

Ho SV, Sheridan PW, Athmer CJ, Heitkamp MA, Brackin JM, Weber D, Brodsky PH (2002) Integrated in situ soil remediation technology: the lasagna process. Environ Sci Technol 29(10):2528–2534

Huang D-Y, Zhou S-G, Chen Q, Zhao B, Yuan Y, Zhuang L (2011) Enhanced anaerobic degradation of organic pollutants in a soil microbial fuel cell. Chem Eng J 172:647–653

Huang D, Guo S, Li T, Wu B (2013) Coupling interactions between electrokinetics and bioremediation for pyrene removal from soil under polarity reversal conditions. CLEAN – Soil, Air, Water 41(4):383–389

Kaku N, Yonezawa N, Kodama Y, Watanabe K (2008) Plant/microbe cooperation for electricity generation in a rice paddy field. Appl Microbiol Biotechnol 79:43–49

Kanagasabi S, Kang YL, Manickam M, Ibrahim S, Pichiah S (2012) Intimate coupling of electro and biooxidation of tannery wastewater. Desalin Water Treat 51:34–36

Ko S-O, Schlautman MA, Carraway ER (2000) Cyclodextrin-enhanced electrokinetic removal of phenanthrene from a model clay soil. Environ Sci Technol 34(8):1535–1541

Lee H-S, Lee K (2001) Bioremediation of diesel-contaminated soil by bacterial cells transported by electrokinetics. J Microb Biotechnol 11:1038–1045

Lee K-Y, Kim K-W (2010) Heavy metal removal from shooting range soil by hybrid electrokinetics with bacteria and enhancing agents. Environ Sci Technol 44(24):9482–9487

Li W-W, Yu H-Q (2015) Stimulating sediment bioremediation with benthic microbial fuel cells. Biotechnol Adv 33:1–12

Li XY, Ding F, Lo PSY, Sin SHP (2002) Electrochemical disinfection of saline wastewater effluent. J Environ Eng 128(8):697–704

Li X, Wang X, Zhang Y, Cheng L, Liu J, Li F, Gao B, Zhou Q (2014) Extended petroleum hydrocarbon bioremediation in saline soil using Pt-free multianodes microbial fuel cells. RSC Adv 4(104):59803–59808

Lin C-W, Wu C-H, Chiu Y-H, Tsai S-L (2014) Effects of different mediators on electricity generation and microbial structure of a toluene powered microbial fuel cell. Fuel 125:30–35

Logan BE, Rabaey K (2012) Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies. Science 337(6095):686–690

Lohner ST, Katzoreck D, Tiehm A (2008) Electromigration of microbial electron acceptors and nutrients: (I) Transport in synthetic media. J Environ Sci Health A 43(8):913–921

Lohner ST, Tiehm A (2009) Application of electrolysis to stimulate microbial reductive pce dechlorination and oxidative VC biodegradation. Environ Sci Technol 43(18):7098–7104

Lovley DR (2006) Bug juice: harvesting electricity with microorganisms. Nat Rev Microbiol 4(7):497–508

Lu L, Huggins T, Jin S, Zuo Y, Ren ZJ (2014a) Microbial metabolism and community structure in response to bioelectrochemically enhanced remediation of petroleum hydrocarbon-contaminated soil. Environ Sci Technol 48(7):4021–4029

Lu L, Yazdi H, Jin S, Zuo Y, Fallgren PH, Ren ZJ (2014b) Enhanced bioremediation of hydrocarbon-contaminated soil using pilot-scale bioelectrochemical systems. J Hazard Mater 274:8–15

Luo Q, Zhang X, Wang H, Qian Y (2005) The use of non-uniform electrokinetics to enhance in situ bioremediation of phenol-contaminated soil. J Hazard Mater 121(1-3):187–194

Maillacheruvu KY, Chinchoud PR (2011) Electrokinetic transport of aerobic microorganisms under low-strength electric fields. J Environ Sci Health A 46(6):589–595

Mao X, Wang J, Ciblak A, Cox EE, Riis C, Terkelsen M, Gent DB, Alshawabkeh AN (2012) Electrokinetic-enhanced bioaugmentation for remediation of chlorinated solvents contaminated clay. J Hazard Mater 213-214:311–317

Mao D, Lu L, Revil A, Zuo Y, Hinton J, Ren ZJ (2016) Geophysical monitoring of hydrocarbon-contaminated soils remediated with a bioelectrochemical system. Environ Sci Technol 50:8205–8213

Maszenan AM, Liu Y, Ng WJ (2011) Bioremediation of wastewaters with recalcitrant organic compounds and metals by aerobic granules. Biotechnol Adv 29(1):111–123

Maymó-Gatell X, Nijenhuis I, Zinder SH (2001) Reductive dechlorination of *cis*-1,2- dichloroethene and vinyl chloride by “*Dehalococcoides ethenogenes*”. Environ Sci Technol 35:516–521

Megharaj M, Ramakrishnan B, Venkateswarlu K, Sethunathan N, Naidu R (2011) Bioremediation approaches for organic pollutants: a critical perspective. Environ Int 37(8):1362–1375

Mena E, Rubio P, Cañizares P, Villaseñor J, Rodrigo MA (2012) Electrokinetic transport of diesel-degrading microorganisms through soils of different textures using electric fields. J Environ Sci Health A 47(2):274–279

Mohan SV, Chandrasekhar K (2011) Self-induced bio-potential and graphite electron accepting conditions enhances petroleum sludge degradation in bio-electrochemical system with simultaneous power generation. Bioresour Technol 102(20):9532–9541

Morris JM, Jin S (2008) Feasibility of using microbial fuel cell technology for bioremediation of hydrocarbons in groundwater. J Environ Sci Health A 43(1):18–23

Morris JM, Jin S (2012) Enhanced biodegradation of hydrocarbon-contaminated sediments using microbial fuel cells. J Hazard Mater 213–214:474–477

Morris JM, Jin S, Crimi B, Pruden A (2009) Microbial fuel cell in enhancing anaerobic biodegradation of diesel. Chem Eng J 146(2):161–167

Mrozik A, Piotrowska-Seget Z (2010) Bioaugmentation as a strategy for cleaning up of soils contaminated with aromatic compounds. Microbiol Res 165(5):363–375

Mulligan CN (2005) Environmental applications for biosurfactants. Environ Pollut 133(2):183–198

Pazos M, Plaza A, Martín M, Lobo MC (2012) The impact of electrokinetic treatment on a loamy-sand soil properties. Chem Eng J 183:231–237

Pham H, Boon N, Marzorati M, Verstraete W (2009) Enhanced removal of 1,2-dichloroethane by anodophilic microbial consortia. Water Res 43:2936–2946

Rabaey K, Keller J (2008) Microbial fuel cell cathodes: from bottleneck to prime opportunity? Water Sci Technol 57(5):655–659

Rakoczy J, Feisthauer S, Wasmund K, Bombach P, Neu TR, Vogt C, Richnow HH (2013) Benzene and sulfide removal from groundwater treated in a microbial fuel cell. Biotechnol Bioeng 110:3104–3113

Rivett MO, Thornton SF (2008) Monitored natural attenuation of organic contaminants in groundwater: principles and application. Proc Inst Civ Eng Water Manage 161(6):381–392

Saichek RE, Reddy KR (2003) Effect of pH control at the anode for the electrokinetic removal of phenanthrene from kaolin soil. Chemosphere 51(4):273–287

Saichek RE, Reddy KR (2005) Surfactant-enhanced electrokinetic remediation of polycyclic aromatic hydrocarbons in heterogeneous subsurface environments. J Environ Eng Sci 4(5):327–339

Saxena G, Bharagava RN (2016) Ram Chandra: advances in biodegradation and bioremediation of industrial waste. Clean Techn Environ Policy 18:979–980

Saxena G, Bharagava RN (2017) Organic and inorganic pollutants in industrial wastes, their ecotoxicological effects, health hazards and bioremediation approaches. In: Bharagava RN (ed) Environmental pollutants and their bioremediation approaches, 1st edn. CRC Press/Taylor & Francis Group, Boca Raton, pp 23–56

Saxena G, Bharagava RN (2019) Bioremediation of industrial waste for environmental safety: industrial waste and its management, 1st edn. Springer, Singapore. https://doi.org/10.1007/978-981-13-1891-7

Saxena G, Purchase D, Mulla SI, Saratale GD, Bharagava RN (2019a) Phytoremediation of heavy metal-contaminated sites: eco-environmental concerns, field studies, sustainability issues and future prospects. Rev Environ Contam Toxicol. https://doi.org/10.1007/398_2019_24

Saxena G, Kishor R, Purchase D, Bharagava RN (2019b) Chandra R, Dubey NK, Kumar V: Phytoremediation of environmental pollutants. Environ Earth Sci 78(14)

Schamphelaire LDE, Van den Bossche L, Dang HS, Höfte M, Boon N, Rabaey K, Verstraete W (2008) Microbial fuel cells generating electricity from rhizodeposits of rice plants. Environ Sci Technol 42:3053–3058

Semple KT, Doick KJ, Jones KC, Burauel P, Craven A, Harms H (2004) Peer reviewed: defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. Environ Sci Technol 38(12):228A–231A

Shantaram A, Beyenal H, Veluchamy RRA, Lewandowski Z (2005) Wireless Sensors Powered by Microbial Fuel Cells. Environ Sci Technol 39(13):5037–5042

Shi L, Müller S, Loffhagen N, Harms H, Wick LY (2007) Activity and viability of polycyclic aromatic hydrocarbon-degrading Sphingomonas sp. LB126 in a DC-electrical field typical for electrobioremediation measures. Microb Biotechnol 1(1):53–61. https://doi.org/10.1111/j.1751-7915.2007.00006.x

Simoni SF, Schäfer A, Harms H, Zehnder AJB (2001) Factors affecting mass transfer limited biodegradation in saturated porous media. J Contam Hydrol 50(1–2):99–120

Sturman PJ, Stewart PS, Cunningham AB, Bouwer EJ, Wolfram JH (1995) Engineering scale-up of in situ bioremediation processes: a review. J Contam Hydrol 19(3):171–203

Suni S, Malinen E, Kosonen J, Silvennoinen H, Romantschuk M (2007) Electrokinetically enhanced bioremediation of creosote-contaminated soil: laboratory and field studies. J Environ Sci Health A 42(3):277–287

Teng Y, Shen Y, Luo Y, Sun X, Sun M, Fu D, Li Z, Christie P (2011) Influence of Rhizobium meliloti on phytoremediation of polycyclic aromatic hydrocarbons by alfalfa in an aged contaminated soil. J Hazard Mater 186(2–3):1271–1276

Tiehm A, Lohner ST, Augenstein T (2009) Effects of direct electric current and electrode reactions on vinyl chloride degrading microorganisms. Electrochim Acta 54(12):3453–3459

Tiehm A, Augenstein T, Ilieva D, Schell H, Weidlich C, Mangold K-M (2010) Bio-electro-remediation: electrokinetic transport of nitrate in a flow-through system for enhanced toluene biodegradation. J Appl Electrochem 40(6):1263–1268

Trombly J (2008) Electrochemical remediation takes to the field. Environ Sci Technol 28(6):289A–291A

Tront JM, Fortner JD, Plötze M, Hughes JB, Puzrin AM (2008) Microbial fuel cell biosensor for in situ assessment of microbial activity. Biosens Bioelectron 24(4):586–590

Venkidusamy K, Megharaj M, Marzorati M, Lockington R, Naidu R (2016) Enhanced removal of petroleum hydrocarbons using a bioelectrochemical remediation system with precultured anodes. Sci Total Environ 539:61–69

Virkutyte J, Sillanpää M, Latostenmaa P (2002) Electrokinetic soil remediation — critical overview. Sci Total Environ 289(1–3):97–121

Wang AJ, Cheng HY, Liang B, Ren NQ, Cui D, Lin N, Kim BH, Rabaey K (2011) Efficient reduction of nitrobenzene to aniline with a biocatalyzed cathode. Environ Sci Technol 45:10186–10193

Wang H, Luo H, Fallgren PH, Jin S, Ren ZJ (2015) Bioelectrochemical system platform for sustainable environmental remediation and energy generation. Biotechnol Adv 33:317–334

Weelink SAB, van Eekert MHA, Stams AJM (2010) Degradation of BTEX by anaerobic bacteria: physiology and application. Rev Environ Sci Biotechnol 9(4):359–385

Wei M, Harnisch F, Vogt C, Ahlheim J, Neu TR, Richnow HH (2015) Harvesting electricity from benzene and ammonium-contaminated groundwater using a microbial fuel cell with an aerated cathode. RSC Adv 5(7):5321–5330

West KA, Johnson DR, Hu P, DeSantis TZ, Brodie EL, Lee PKH, Feil H, Andersen GL, Zinder SH, Alvarez-Cohen L (2008) Comparative genomics of "Dehalococcoides ethenogenes" 195 and an enrichment culture containing Unsequenced "Dehalococcoides" strains. Appl Environ Microbiol 74(11):3533–3540

Wick LY, Mattle PA, Wattiau P, Harms H (2004) Electrokinetic transport of PAH-degrading bacteria in model aquifers and soil. Environ Sci Technol 38(17):4596–4602

Wick LY, Shi L, Harms H (2007) Electro-bioremediation of hydrophobic organic soil-contaminants: a review of fundamental interactions. Electrochim Acta 52(10):3441–3448

Williams KH, Nevin KP, Franks A, Englert A, Long PE, Lovley DR (2010) Electrode-based approach for monitoring in situ microbial activity during subsurface bioremediation. Environ Sci Technol 44(1):47–54

Wu X, Alshawabkeh AN, Gent DB, Larson SL, Davis JL (2007) Lactate transport in soil by DC fields. J Geotech Geoenviron 133(12):1587–1596

Wu MZ, Reynolds DA, Fourie A, Thomas DG (2013) Optimal field approaches for electrokinetic in situ oxidation remediation. Ground Water Monit Remediat 33(1):62–74

Xu W, Wang C, Liu H, Zhang Z, Sun H (2010) A laboratory feasibility study on a new electrokinetic nutrient injection pattern and bioremediation of phenanthrene in a clayey soil. J Hazard Mater 184(1–3):798–804

Yan F, Reible D (2015) Electro-bioremediation of contaminated sediment by electrode enhanced capping. J Environ Manag 155:154–161

Yan Z, Song N, Cai H, Tay J-H, Jiang H (2012) Enhanced degradation of phenanthrene and pyrene in freshwater sediments by combined employment of sediment microbial fuel cell and amorphous ferric hydroxide. J Hazard Mater 199–200:217–225

Yan Z, Jiang H, Cai H, Zhou Y, Krumholz LR (2015) Complex interactions between the macrophyte acorus calamus and microbial fuel cells during pyrene and benzo[a]pyrene degradation in sediments. Sci Rep 5(1)

Yuan Y, Guo S-H, Li F-M, Li T-T (2013) Effect of an electric field on n-hexadecane microbial degradation in contaminated soil. Int Biodeterior Biodegr 77:78–84

Zhang T, Gannon SM, Nevin KP, Franks AE, Lovley DR (2010) Stimulating the anaerobic degradation of aromatic hydrocarbons in contaminated sediments by providing an electrode as the electron acceptor. Environ Microbiol 12(4):1011–1020

Zhang T, Bain TS, Barlett MA, Dar SA, Snoeyenbos-West OL, Nevin KP, Lovley DR (2014) Sulfur oxidation to sulfate coupled with electron transfer to electrodes by Desulfuromonas strain TZ1. Microbiology 160(Pt_1):123–129

Zhang Y, Wang X, Li X, Cheng L, Wan L, Zhou Q (2015) Horizontal arrangement of anodes of microbial fuel cells enhances remediation of petroleum hydrocarbon-contaminated soil. Environ Sci Pollut Res 22(3):2335–2341

15

Electrochemical Methods for the Detection of Toxic As(III) and As(V) from Natural Water

Mohammad Hasnat, Nahida Tanjila,
Md. Musfiqur Rahman, and Mohammed M. Rahman

Abstract

The aim of this chapter is to bring out the determination of arsenic in natural water under electrochemical techniques. Arsenite [As(III)] and arsenate [As(v)] are two predominant forms of arsenic that cause health concerns due to their significant toxicity and worldwide presence in drinking water and groundwater. The major sources of arsenic pollution may be natural process such as dissolution of arsenic-containing minerals and anthropogenic activities such as percolation of water from mines, etc. Among the countries facing arsenic contamination problems, Bangladesh is the most affected. Up to 77 million people in Bangladesh have been exposed to toxic levels of arsenic from drinking water. Therefore, it has become an urgent need to provide arsenic-free drinking water in rural households throughout Bangladesh. This chapter reveals the detection techniques and catalytic activity of different modified electrodes. Electrode surface modification with metallic nanoparticles (NPs) and carbonaceous nanomaterials (carbon nanotubes) can improve detection sensitivity and selectivity by circumventing the interferences from various endogenous metals or organic compounds in water. Numerous publications have been published to develop sensitive, reproducible and economically cheap sensor in the electrochemical field. In case of all the electrochemical methods, the detection limit is below the World Health Organization guideline value of 10 ppb (133.3 nM).

M. Hasnat (✉) · N. Tanjila · M. M. Rahman
Department of Chemistry, Shahjalal University of Science & Technology, Sylhet, Bangladesh
e-mail: mah-che@sust.edu

M. M. Rahman (✉)
Department of Chemistry & Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, Jeddah, Saudi Arabia
e-mail: mmrahman@kau.edu.sa

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_15

Keywords
Arsenic pollutant · Electrochemical method · Metallic nanoparticles · Carbon nanotubes · Detoxification · Cyclic voltammetry · Sensors · Environmental safety

15.1 Literature Survey

Arsenic is ranked as twentieth in abundance among the elements in the earth's crust, a poisonous chemical that is widely distributed in nature and occurs in the form of an inorganic or organic compound. It can exist in four valence states: −3, 0, +3 and + 5 (Majid et al. 2006). The two predominant species of arsenic are arsenate [As (V)] and arsenite [As(III)]. Under reducing conditions, arsenite [As (III)] is the dominant form that is mobile. In addition, the inorganic compounds usually consist of soluble [As (III)] (Moonis Ali and Yuh 2011). Arsenite [As (III)] is 50 times more toxic than arsenate [As (V)] due to its reactions with enzymes in human metabolism. As (V) is less toxic and can occur as either free, inorganic or organic compound (Abdollah et al. 2008). Depending on pH, there are four different forms of As (III) and As (V): H_3AsO_3, H_2AsO_3, $HAsO_3^{2-}$ and AsO_3^{3-} vs. H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}. Arsenic in aqueous solutions mainly presents as $HAsO_4^{2-}$ and $H_2AsO_4^-$ and, most likely, partially as H_3AsO_4, AsO_4^{3-} or H_2AsO^{3-} (Luong et al. 2014a). Since inorganic arsenic is one of the most axiomatic carcinogens, it affects the malformations. Generally, it affects the neural tube in animals and contributes to human birth defects (U.S. Environmental Protection Agency 1994). The source of arsenic contaminant is ground water, and it directly comes into the human body by drinking water (Nahida et al. 2016). Commercially, arsenic is used as pesticides such as lead arsenate, calcium arsenate, monosodium methane arsonate, disodium methane arsonate, etc. in cotton production, e.g. cacodylic acid, and in the manufacture of glass, paper and semiconductors (Moonis Ali and Yuh 2011). As a result, they enter into natural water systems from the earth's crust or from industrial and agricultural wastes (Andreae 1979). Long-term exposure to arsenic via drinking water is causally related to increased risks of cancer in the skin, lungs, bladder and kidney, as well as other skin diseases such as hyperkeratosis and pigmentation changes. An estimated Bangladeshi population of 65 million is exposed to arsenic poisoning through drinking water (Takahashi et al. 2011) since groundwater arsenic levels in some locations can reach 2 mg/L (Hrapovic et al. 2007a). The World Health Organization's (WHO) maximum permissible contaminant level of arsenic in drinking water is 10 ppb (Abedin et al. 2002; World Health Organization 2004; U.S. Environmental Protection Agency 2007). Concerning toxicity, the detection of arsenic has become a matter of interest nowadays. However, a vast number of existing methods are suitable for laboratory conditions only. In these cases, analysis is time consuming and not suitable for routine monitoring of large numbers of samples. Therefore, to solve these problems, a rapid portable sensor needs to be developed. The use of electrochemical methodologies has recently come to the forefront of research as a possible means of fulfilling these requirements. Many electrochemical and spectroscopic experiments have been performed to detect total arsenic in waste water (Bauer et al. 2001; Korolczuk et al. 2015; Dhillon et al. 2015; Luong et al. 2014b; Zaggout et al. 2007; Suna et al. 2011; Schumacher et al. 2011; Francesconi and Kuehnelt 2004; Ito et al. 2010; Wood and McKenna 1962). In the electrochemical process, the detection of arsenic is based on the detection of the two predominant forms of arsenic, i.e. arsenite (III) and arsenate (V). As (III) is uncharged at neutral pH, while As (V) is negatively charged. The groundwater pH is often between 6 and 8; thus As (III) is more mobile than As (V) because the movement of As (V) is retarded by its electrostatic attraction to positively charged particles, e.g. iron hydroxides (Domenico and Schwartz 1998a). However, the detection of arsenite is quite easy with respect to arsenate. Arsenite has an oxidation state +3 and can be transformed from As (III) to As (V) by a conventional electrode such as platinum, glassy carbon, gold, etc. whereas As (V) is electro-inactive and direct electrochemical determination of As (V) in neutral pH water is considered impossible (Gibbon-Walsh et al. 2012). Nevertheless, the detection of As (V) has been performed by many researchers following a chemical-electrochemical (CE) mechanism. In CE mechanism, As (V) is chemically reduced to As (III) by reducing agents. Thereby the electrochemical determination of total arsenic has been established.

The kinetics of the electrocatalytic oxidation of As (III) were studied at a Pt disk electrode by using cyclic voltammetry, convolution potential sweep voltammetry and electro-chemical impedance spectroscopy (Mohammad Abul et al. 2016). The interferences of industrial dyes in the determination of arsenic is also a matter of concern. The interferences of arsenite ions on electrocatalytic oxidation of alizarin red s (ARS) was studied using Pt and ITO electrodes (Nahida et al. 2016). The electrochemical determination of As (V) in natural waters of neutral pH including seawater has been investigated by anodic stripping voltammetry (ASV) using a manganese-coated gold microwire electrode (Gibbon-Walsh et al. 2012).

15.2 Electrochemical Technique

Electroanalytical methods are a class of techniques in analytical chemistry which study an analyte by measuring the potential (volts) and/or current (amperes) in an electrochemical cell containing the analyte. These methods can be broken down into several categories depending on which aspects of the cell are controlled and which are measured. The three main categories are potentiometry (the difference in electrode potentials is measured), coulometry (the cell's current is measured over time) and voltammetry (the cell's current is measured while actively altering the cell's potential) (Fig. 15.1).

15.2.1 Cyclic Voltammetry

In typical cyclic voltammetry, a solution component is electrolysed (oxidized or reduced) by placing the solution in contact with an electrode surface and then

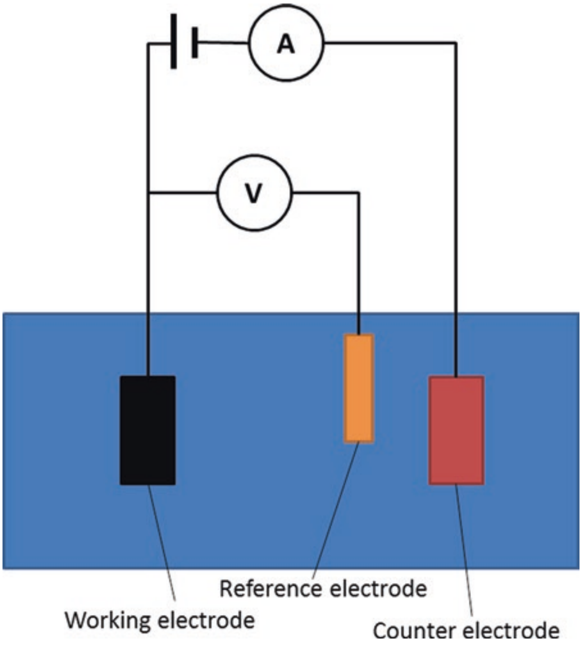


Fig. 15.1 A schematic voltammetric set up

making that surface sufficiently positive or negative in voltage to force electron transfer. The investigated surface is the working electrode which is placed into the electrolyte. The electric current goes between the working and the counter electrode. The voltage on working electrode is set according to the reference electrode. The reference electrode is usually made from calomel or Ag/AgCl. The counter electrode is usually made of Pt wire. The working electrode can be made of various materials like glassy carbon, carbon paste, Au, Pt, Pd, Ag, etc. that are coated with investigated catalytic powder. The measurements are performed that the voltage at working electrode is related to the reference electrode that is periodically cycled between two values using potentiostat. The first half of the cycle is a forward scan and it is increasing, and the second part of cycle is a reverse scan and it is decreasing. The sweep rate is generally from 10 to 200 mV/s. The results are plotted as current against voltage, and it is called a voltammogram (see Fig. 15.2).

15.2.2 Stripping Voltammetry (SV)

SV is a popular and powerful technique for trace metal analysis. Stripping voltammetry comprises a group of various techniques including anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV) and adsorptive stripping voltammetry (AdSV). It is an ultrasensitive detection technique based on electrochemical measurements similar to polarography. The process involves electrochemical deposition of trace metals on a suitable electrode for a few minutes at pertinent

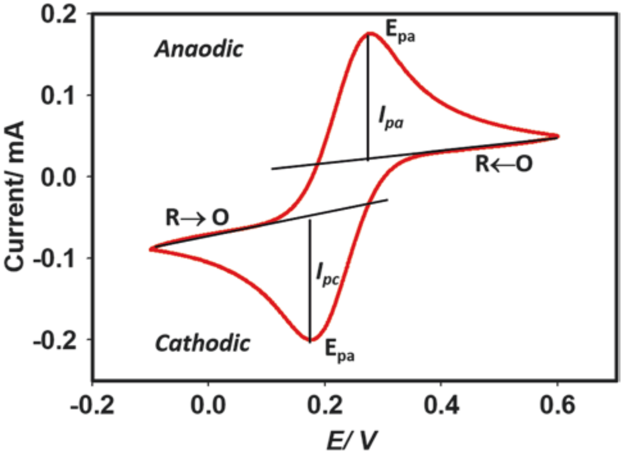


Fig. 15.2 The resulting cyclic voltammogram showing the measurement of the peak currents and peak potentials

reduction potentials and then the oxidation of the metal back into solution by a reverse potential scan (linear, differential, pulse or square). Stripping voltammetry is a two-step technique that allows simultaneous detection of various inorganic and organic species in the sub-nanomolar range. The first step consists of the electrolytic deposition of a chemical species onto an inert electrode surface at a constant potential. This preconcentration step explains the remarkable sensitivity of the technique. The second step consists of the application of a voltage scan to the electrode. At a specific potential, it causes the stripping of a specific species accumulated onto the electrode surface as amalgam or thin films into the solution. The resulting faradic current is proportional to the concentration of the chemical species (see Fig. 15.3).

Trushina and Kaplin (1970; Kaplin et al. 1973) established the anodic stripping voltammetry technique for trace arsenic analysis, which is based on the deposition of metal arsenic on the electrode surface with subsequent anodic stripping (Scheme 15.1).

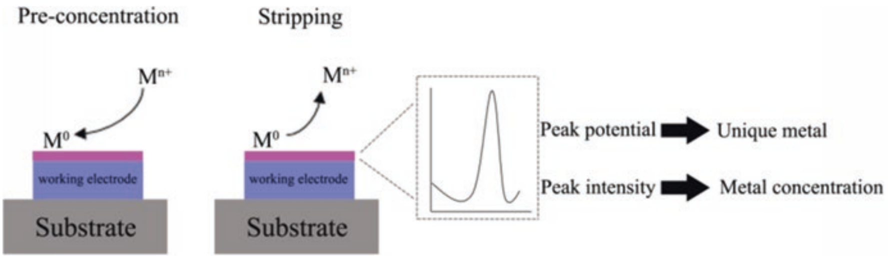


Fig. 15.3 Anodic stripping voltammetry (ASV) principle

$$\textbf{\textit{Deposition:}}\ As^{3+} + 3e^{-} \rightarrow As^{0}$$

$$\textbf{\textit{Stripping:}}\ As^{0} \rightarrow As^{3+} + 3e^{-}$$

Scheme 15.1 Processes occur during anodic stripping voltammetry

Most cathodic stripping techniques are carried out by using a HMDE, as this electrode does not suffer from the disadvantages of the solid electrodes, such as the response being dependent on past history or the formation of oxide films. However, anodic stripping of arsenic using a HMDE is not analytically useful due to interference from the oxidation of mercury (Myers and Osteryoung 1973). Cathodic stripping analysis of arsenic at the HMDE is based on arsenic preconcentration in highly acidic media with further scanning in the cathodic direction to obtain a peak due to the formation of arsine (Holak 1980). In order to increase sensitivity, intermetallic complexes of arsenic are stripped from HMDE, whereby As (III) reacts with copper (Sadana 1983; Li and Smart 1996) or selenium (Holak 1980) to form the relevant complex, which can be stripped cathodically (Scheme 15.2 and Fig. 15.4).

15.2.3 Principle of Hanging Mercury Drop Electrode (HMDE)

The earliest voltammetric techniques, including polarography, used mercury for the working electrode. Since mercury is a liquid, the working electrode often consists of a drop suspended from the end of a capillary tube. Hanging mercury drop electrode is an electrode in which a drop of Hg is suspended from a capillary tube. In the hanging mercury drop electrode, or HMDE, a drop of the desired size is formed by the action of a micrometer screw that pushes the mercury through a narrow capillary tube (see Fig. 15.5).

The solid electrode is placed in a solution of Hg^{2+} and held at a potential at which the reduction of Hg^{2+} to Hg is favourable, forming a thin mercury film. Mercury has several advantages as a working electrode. Perhaps the most important advantage is its high overpotential for the reduction of H_3O^+ to H_2, which allows for the application of potentials as negative as −1 V versus the SCE in acidic solutions, and − 2 V versus the SCE in basic solutions. A species such as Zn^{2+}, which is difficult to reduce at other electrodes without simultaneously reducing H_3O^+, is easily reduced at a mercury working electrode. Other advantages include the ability of metals to dissolve in the mercury, resulting in the formation of an amalgam, and the ability to easily renew the surface of the electrode by extruding a new drop. One limitation to its use as a working electrode is the ease with which Hg is oxidized. For this reason,

$$\textbf{\textit{Deposition:}}\ 2As^{3+} + 3MHg + 6e^{-} \rightarrow M_3As_2 + 3Hg$$

$$\textbf{\textit{Stripping:}}\ M_3As_2 + 12H^{+} + 12e + 3Hg \rightarrow AsH_3 + H_2 + 3MHg$$

$$M = Cu\ \text{or}\ Se$$

Scheme 15.2 Processes occur during cathodic stripping voltammetry

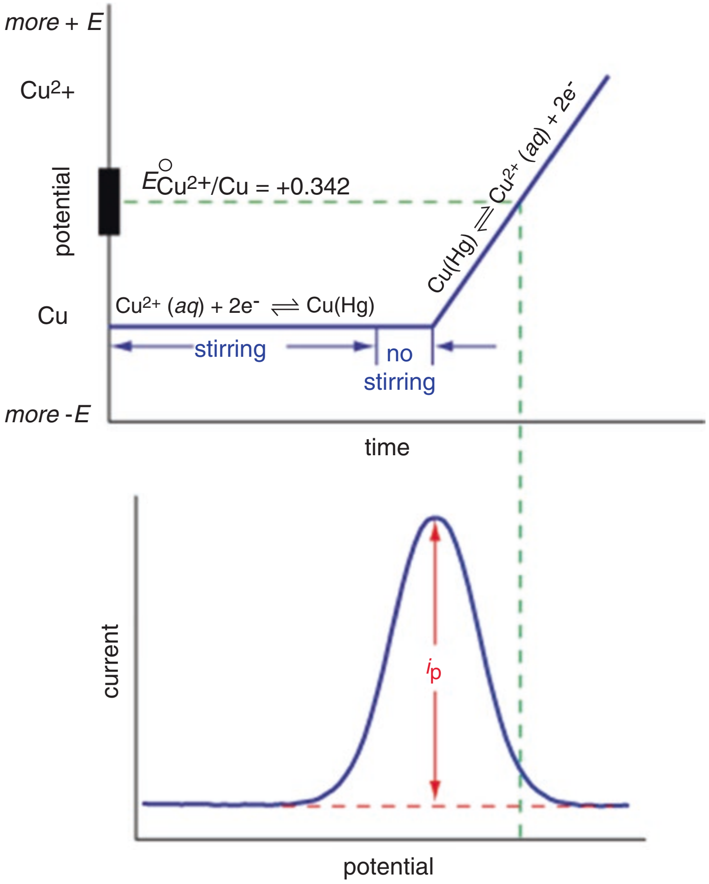


Fig. 15.4 A typical anodic stripping voltammogram at a hanging mercury drop or a mercury film electrode (in this case the reduction of Cu^{2+} to Cu, which forms an amalgam with Hg)

mercury electrodes cannot be used as at potentials more positive than −0.3 V to +0.4 V versus the SCE, depending on the composition of the solution.

15.3 Electrochemical Detection of Arsenite (As^{3+})

GC electrode is preferred commonly as a working electrode for the electrochemical detection of As (III) because it is quite cheap and is easily refreshed with the electrode surface. The overpotentials of water oxidation and reduction on GC electrode are very high, and therefore you have a wide electrochemical window. Dai and Compton (2006a) used platinum nanoparticle modified glassy carbon electrodes to detect As (III) without the interference of copper. Majid et al. (2006) prepared gold nanoparticle modified glassy carbon electrode for the electrochemical

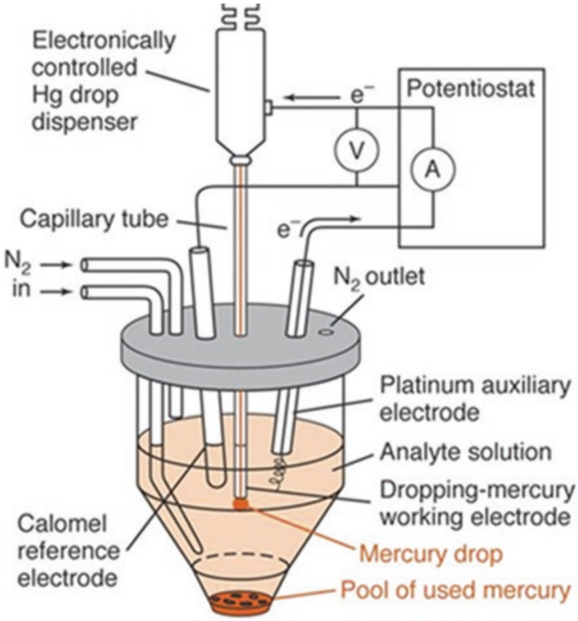


Fig. 15.5 Polarography apparatus featuring a HDME

determination of arsenite. Abdollah et al. (2008) also used glassy carbon electrodes modified with cobalt oxide nanoparticles for the electrochemical detection of trace amount of As (III). Dai and Compton (2006a) performed the cyclic voltammetric responses of As (III) additions to 0.1 M H_2SO_4 in the range from 0.2 V to +1.3 V (vs. SCE, 100 mVs^{-1}) of a platinum nanoparticle modified electrode prepared by applying 25 potential cycles stepped to +0.5 V for 0.01 s then to 20.7 V for 10s from 0.1 M KCl containing 1 mM $PtCl_6^{2-}$. The oxidation of As (III) to As (V) was observed at ca. +0.85 V (vs. SCE). They proposed that the reaction is likely electrocatalysed by the formation of PtOH on the electrode (Wang et al. 2000; Abdollah et al. 2004). The following mechanism was suggested for oxide-free surface (Abdollah et al. 2004):

$$\mathrm{Pt + H_2O = PtOH + H^+ + e}$$

$$\mathrm{PtOH + As(OH)_3 = PtOHAs(OH)_3}$$

$$\mathrm{PtOHAs(OH)_3 = PtOAs(OH)_3 + H^+ + e}$$

$$\mathrm{PtOAs(OH)_3 \rightarrow Pt + OAs(OH)_3}$$

In order to compare the results from the platinum macroelectrode and the platinum nanoparticle modified electrode, current densities were used for the comparison. The current densities were higher on the platinum nanoparticle modified GC electrode than on the platinum macroelectrode indicating that the platinum nanoparticle modified GC electrode results in better sensitivity than the platinum macroelectrode. The interferences of copper (II) chloride ion with the detection of As (III) were studied using cyclic voltammetry. It was found that Cu (II) and chloride ion has no considerable interferences to the oxidation peak of As (III). The calibration slope was 0.22 AM^{-1} and the LOD ($S/N = 3$) (Wood and McKenna 1962) was calculated to be 0.028 ± 0.003 μM (2.1 ± 0.23 ppb) whereas for a platinum macroelectrode (geometric area of 0.07 cm^2) with the same method, the LOD was 0.48 ± 0.02 μM (35 ± 1.5 ppb). Considerable (Liza et al. 2008a) attention has been paid to porous gold materials for applications including catalysis (Haruta 2007), fuel cells (Yi et al. 2004) and energy storage (Gregory et al. 2002) and for the development of chemical sensors (Hieda et al. 2004; Li et al. 2007; Kristien et al. 2004; Shulga et al. 2007). Majid et al. (2006) prepared gold nanoparticle modified GC electrode by electrodepositing gold nanoparticles (0.1 mM $HAuCl_4$ in 0.5 M H_2SO_4) on the cleaned dual GC electrode surface by applying a potential of 0.18 V for 15 s (reduction of Au^{3+} to the element Au^0) (Sabahudin et al. 2003). The resulting electrode surface was characterized by SEM and AFM. The arsenite concentrations with respect to gold nanoparticle deposition characterization were performed by anodic stripping square wave voltammetry, frequency (10–110 Hz), increment (0.01–0.05 V), amplitude (0.01–0.10 V), deposition potential (−0.5 to −0.1 V) and deposition time (60–900 s) as well as flow rate (0.17–1.12 mL/min) and gasket size and number. The characteristic peak for arsenite was observed at ~0.25 V. The electrochemical system was linear up to 15 ppb with a detection limit of 0.25 ppb. For comparison, arsenite determination experiments were also conducted on the dual bare GC (without gold nanoparticle deposition) and dual bare gold electrodes. The dual GC electrode did not respond to arsenite even at concentrations as high as 100 ppb. Although the dual bare gold electrode responded well to arsenite, the response was only ~25% of that obtained with the gold nanoparticle modified GC electrode. The increase in sensitivity to arsenite could be attributed to the larger resulting gold surface area when the gold nanoparticles were deposited on the GC substrate. Abdollah et al. (2008) prepared a novel cobalt oxide nanoparticle-based sensor for the detection of trace amount of As^{3+} ion in aqueous solution. Cobalt oxyhydroxide film was electrodeposited on the surface of glassy carbon electrode from 1 mM cobalt chloride pH 7 PBS, using repetitive potential cycling (30 cycles at 100 mVs^{-1}) between 1.2 and − 1.1 Vin alkaline solution without cobalt ions. Characterization of cobalt oxide nanoparticles was performed by SEM, EDS. The electrode surface was checked by recording cyclic voltammograms of the modified electrode (Innocenzo 2002; Jafarian et al. 2003). The electro-catalytic activity of the modified electrode for arsenic was carried out by modified and unmodified electrodes in the absence and presence of As^{3+} (70.0 mM) at pH 7 buffer solution at potential range -1.1 to 1.1 V. For bare glassy carbon electrode, no redox response of As^{3+} can be seen in the potential range from 0.4 to 1.1 V. However, at the co-oxide modified GC electrode, the oxidation current of cobalt oxide film was greatly increased due to catalytic oxidation of arsenic. The overvoltage was decreased, and the increased peak current of As^{3+} oxidation due to the cobalt oxide nanoparticles has high catalytic ability for arsenic oxidation based on the obtained results. The following catalytic scheme describes the reaction sequence in the oxidation of As^{3+} with cobalt oxide nanoparticles:

$$Co_3O_4 + H_2O + OH- \rightarrow 3CoOOH + e^-$$

$$6CoOOH + As^{3+} + 2H^+ \rightarrow K_{cat}\,2Co_3O_4 + As^{5+} + 4H_2O$$

In addition, cyclic voltammetry, a much more current sensitive amperometric detection under stirred condition, was employed in order to estimate the low detection limit of the rotated modified electrode (2000 rpm) with successive injection of As^{3+}(200 nM and 3 μM) at an applied potential 0.75 V versus the reference electrode. The linear least squares calibration curve over the range of 200–4000 nM (20 points) is I (nA) = 111.3[As^{3+}] + 10.4 nA with a correlation coefficient of 0.9991, and the detection limit (signal to noise of 3) and sensitivity were 11 nM and 111.3 nA/M, respectively. They also showed that when the concentration of Cl^-, SO_4^{2-}, NO_3^-,CO_3^{2-}, PO_4^{3-}, Cu^{2+}, Bi^{3+}, Sn^{2+}, Cr^{3+}, Pb^{2+}, Sb^{2+}, Sb^{3+}, Hg^{2+} and Zn^{2+} co-existing in the sample were 100 times that of As(III), no significant interference could be observed, <1%, indicating that these species did not affect the determination of arsenic. However, for Fe^{2+} at 5–50 fold concentration ratio to arsenic, no significant interferences were observed. When the concentration ratio of Fe^{2+} ion was more than 100 times of As (III), the peak current showed an increase of approximately 3.2%.

The superior properties of high boron-doped diamond (BDD) electrodes compared to conventional carbon electrodes have already been reported, due to their superb electrochemical properties, such as their wide potential window, very small charging current, chemical inertness and mechanical durability (Akane et al. 2007). Hrapovic et al. (2007b) prepared reusable platinum nanoparticle modified boron-doped diamond microelectrodes for oxidative determination of arsenite. Ivandini et al. (Ivandini et al. 2006) reported iridium-implanted boron-doped diamond electrodes for the electrochemical detection of As (III). Rassaei et al. (Liza et al. 2008b) used electroaggregated gold nanoparticles onto boron-doped diamond electrodes for arsenite determination in phosphate media. Hrapovic et al. (Hrapovic et al. 2007b) deposited on the GC and BDD electrodes by electrodepositing 2 mM H_2PtCl_6 in 0.5 mM H_2SO_4 by potential cycling (Dai and Compton 2006a), potentiostatic deposition (Montilla et al. 2003) or multipotential step deposition techniques (Siné 2006). The resulting electrode surface was characterized by SEM and AFM. Platinum salt concentration, deposition time, deposition potential, morphology and characteristics of the starting electrode surface affected the distribution, size and number of platinum nanoparticles deposited on the electrode surfaces during nucleation followed by particle growth. The optimization involved the multipotential step technique (Siné 2006) in 2 mM H_2PtCl_6 supported in 0.5 mM H_2SO_4, prebubbled with nitrogen. Measurement of arsenite concentration with respect to the background electrode surface (GC, BDD macro and microelectrodes) and the Pt nanoparticle size and distribution were performed by LSV at different scan rates using the one-step procedure. During the anodic sweep, the characteristic peak for As (III) to As (V) oxidation (Dai and Compton 2006a; Cabelka et al. 1984a; Kao and Kuwana 1985; Tomilov et al. 2001; Cabelka et al. 1984b) was observed at 0.88 V versus Ag/AgCl. Linear sweep voltammetry performed with the modified BDD microelectrode resulted in very low detecting currents with enhanced signal-to-noise ratios with linearity up to 100 ppb and a detection limit of 0.5 ppb. A comparison of the standard electrochemical stripping technique for As (III) determination using Au nanoparticle modified electrode surfaces (Yuh-Chang et al. 1997; Davis et al. 1978; Dai et al. 2004a; Rosemary and Kounaves 2000; Kopanica and Novotny 2008) and the oxidative determination by the Pt-modified BDD electrode was performed. They found the BDD microelectrode having the superior performance over its macro counterpart since the hemispherical diffusion profile induces an improved mass transfer compared to that of the macroelectrode, resulting in much higher current density, i.e. a high signal-to-noise ratio. The effect of sulphuric, nitric or hydrochloric acid as the supporting electrolyte on the oxidation of As (III) at 100 ppb was studied. The optimal level of all three acids was 0.1 M since increasing acid concentrations beyond this level did not improve detection sensitivity and reproducibility. Sulphuric acid (0.1M) was found the best choice as evident by a maximum peak at 0.88 V versus Ag/AgCl, whereas in hydrochloric acid, the As (III) peak shifted toward a more positive potential, 0.94 V, and was partially masked with the platinum oxide formation. Although nitric acid displayed very stable background current with a lower oxidation potential, the response signal was very weak. Interferences of copper ion were also investigated, and it was found that below 100 ppb Cu (II), the response signal to As(III) was virtually unaffected except for a slight increase in the background current. Only at very high copper concentrations (>600 ppb), the oxidation peak of Cu became pronounced and slightly affected the arsenite determination. The BDD microelectrode was regenerated by the ac electrochemical etching technique (Hrapovic and Luong 2003), allowing its reuse. Ivandini et al. (2006) developed iridium-modified, boron-doped diamond electrodes fabricated by an ion implantation method for electrochemical detection of arsenite (As (III)). Ir + ions were implanted with energy of 800 keV and a dose of 1015 ion cm^{-2}. An annealing treatment at 850 °C for 45 min in H_2 plasma (80 Torr) was required to rearrange metastable diamond produced by an implantation process. The electrodes were characterized by SEM, AFM, Raman and X-ray photoelectron spectroscopy. Electrochemical behaviour of the film was investigated for arsenite oxidation in 0.1 M phosphate buffer solution (PBS) at pH 4 of 1 mM arsenite at the potential range of −0.8 to +1.0 V (vs. Ag/AgCl) at a scan rate of 50 mV/s under cyclic voltammetric process. The electrocatalytic activity was examined in the presence and absence of 1 mM As (III) in buffer solution at as-deposited BDD in comparison with an Ir-BDD and an Ir-wire electrode. Although faradaic response increased, no peak was observed within the potential window of the as-deposited BDD. In contrast, a well-defined couple anodic and cathodic peaks were observed at ~ +0.65 and ~ −0.4 V (vs. Ag/AgCl) at both Ir-wire and Ir-BDD electrodes whereas a strong catalytic effect shown by a decrease in the overall potential and an enhancement of peak current was achieved from arsenite oxidation at the Ir-BDD. Although an enhanced peak current for arsenic oxidation was observed at Ir-wire, its background current was relatively high. The difference between signal current of arsenic oxidation and the background at Ir-wire was not as clear as that at Ir-BDD electrode. The S/B of Ir-BDD is ~221 times higher than that of Ir wire which results in better performance of the electrode in terms of low detection limit. The consecutive scans at a potential range of −0.8 to +1.0 V (vs. Ag/AgCl) show stable oxidation-reduction potentials and current responses of the pair of peaks without any stirring or mixing the solution. These results indicate that a reversible reaction occurred at the electrode surface. They performed a separate experiment of As (V) in the same pH to check whether the peak at ~ −0.45 V (vs. Ag/AgCl) represents As (V) reduction at the modified electrode. A similar peak was obtained at the potential of −0.5 V vs. Ag/AgCl (data not shown). This peak was stable and repeatable at the same potential. However, no oxidation peak was found in the reverse oxidation part, indicating that the As (V) was not reducible back to As (III). To study the reaction mechanism as well as to optimize the experimental condition, the pH variation was investigated in this approach. It was found the excellent electrocatalytic activity of Ir-BDD at pH range 1–6. At pH higher than 6, the oxidation peak disappeared. The reason was probably due to, at higher pH, the increase in negative charge on the surface, while OH^- concentration increased. This condition can start a repulsion effect between $HAsO_2$ and the electrode surface. They proposed an As (III) oxidation mechanism at Ir-BDD similar to the detailed mechanisms that have been reported for As (III) oxidation at Pt electrodes (Williams and Johnson 1992) as follows:

$$\mathrm{HAsO_2 + H_2O \rightarrow OHAsO_2 + 2H^+ + 2e}$$

$$\mathrm{H_2O + IrO_x \rightarrow IrO_{(x+1)}H + H^+ + e}$$

$$\mathrm{HAsO_2 + IrO_{(x+1)}H \rightarrow IrO_x + OHAsO_2 + H^+ + e}$$

The electrodes exhibited high catalytic activity toward As (III) oxidation with the detection limit S/N = 3), sensitivity and linearity of 20 nM (1.5 ppb), 93 nA μM^{-1} cm^{-2}, and 0.999, respectively. The precision for 10 replicate determinations of 50 μM As (III) was 4.56% relative standard deviation. Gold nanoparticle surfaces are sensitive tools for the determination of As (III) in hydrochloric acid (Dai et al. 2004) or in nitric acid media (Baron et al. 2008). Rassaei et al. (Liza et al. 2008b) prepared an electrode by electroaggregation process causing 5 nm diameter gold nanoparticles (in 40 mL volume of aqueous 1 M $NaClO_4$) to deposit cathodically from aqueous solution of gold nanoparticles on BBD electrode. The resulting electrode surface was characterized by electron microscopy and by cyclic voltammetry. The reactivity of electro-aggregated gold nanoparticles was initially experimented in 10 mM As (III) in 0.1 M HNO_3. The most effective optimized deposition potential was found

−0.6 V vs. SCE. The processes during deposition (P1) and anodic stripping (P2) have been reported as follows:

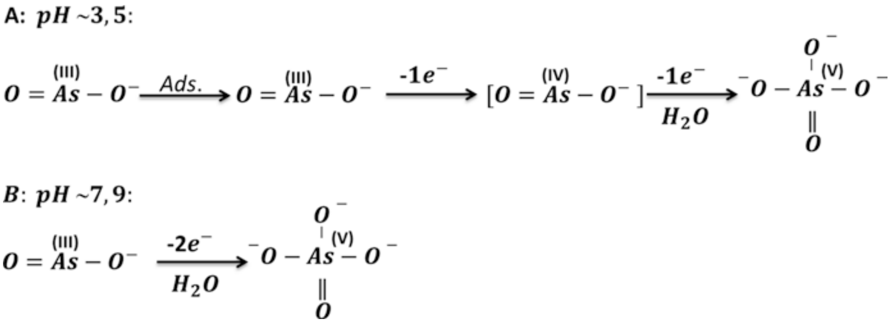
$$\text{P1}: \text{H}_3\text{AsO}_3\left(\text{aq.}\right) + 3\text{H}^+\left(\text{aq.}\right) + 3\text{e}^- \leftrightharpoons \text{As}\left(0\right) + 3\text{H}_2\text{O}\left(\text{aq.}\right)$$

$$\text{P2}: \text{As}\left(0\right) + 3\text{H}_2\text{O}\left(\text{aq.}\right) \leftrightharpoons \text{H}_3\text{AsO}_3\left(\text{aq}\right) + 3\text{H}^+\left(\text{aq}\right) + 3\text{e}-$$

A further more reversible voltammetric process linked to the arsenite redox system can be observed at a potential of −0.18 V vs. SCE. In 0.1 M phosphate buffer pH 5, both oxidation and reduction of arsenite were observed at +0.25 V vs. SCE where the As (III) redox state is stable. The reduction of AsO_3^{3-} (see P1) occurs at a potential −0.44 V vs. SCE and the corresponding stripping response (see P2) is now observed at −0.12 V vs. SCE. The oxidation of arsenite to arsenate at a potential of 0.5 V vs. SCE (see P3) is a well-known two electron process (Rassaei et al. 2008; Abdollah et al. 2008; Hung et al. 2004):

$$\text{P3}: \text{AsO}_3^{\ 3-}\left(\text{aq.}\right) + \text{H}_2\text{O}\left(\text{aq.}\right) \leftrightharpoons \text{AsO}_4^{\ 3-}\left(\text{aq.}\right) + 2\text{H}^+\left(\text{aq.}\right) + 2\text{e}^-$$

The effect of the deposition time on the charge under the stripping response shows an improved anodic stripping voltammetry with the gold nanoparticle deposition time is increased for solutions of As (III) in 0.1 M HNO_3 and in 0.1 M phosphate buffer. In order to investigate the effect of the solution pH on the voltammetric oxidation, reduction and stripping responses, voltammetric data at pH 3 to pH 11 were recorded. Although the stripping peaks slightly improved at more acidic pH, analytical optimization is attempted at the more relevant neutral point at pH 7. Typical detection limits of LOD (3σ) 30 ppb in nitric acid and LOD (3σ) 1 ppb in phosphate buffer (pH 7) are observed. (Dai and Compton 2006b*)* fabricated gold nanoparticles onto indium tin oxide (ITO) film coated glass electrodes through direct electrochemical deposition from 0.5 M H_2SO_4 containing 0.1 mM $HAuCl_4$ (Dai et al. 2004b; Masanori et al. 2003). Cyclic voltammetry was performed in the range from −0.6 V to +0.4 V (vs. SCE, 100 mVs^{-1}) of a gold nanoparticle modified electrode (stepped from 1.055 V to −0.045 V for 300 s from 0.5 M H_2SO_4 containing 0.1 mM $AuCl_4^-$) in 1 M HCl. The reduction wave emerges at −0.35 V (vs. SCE) upon the addition of 1 μM As (III) and can be attributed to the three electron reduction of As (III) to As (0). On the reversal anodic scan, an oxidation wave at +0.25 V (vs. SCE) was observed. This process is ascribed to the subsequent re-oxidation of As (0) to the parent As (III) species. The plots of current densities vs. concentration of As (III) on different gold nanoparticle modified ITO electrode show that increasing the concentration of $AuCl_4^-$ from 0.01 mM to 0.1 mM causes the increase of sensitivity, from 33.4 to 58.8 A cm^{-2} M^{-1}. The highest sensitivity, 0.1 mM $AuCl_4^-$ with 300 s deposition time, was selected as the preparation conditions for the gold nanoparticle modified electrodes used in the following experiments from different



$$\mathbf{A:}\ pH \sim 3,5:\quad O=\overset{(III)}{As}-O^- \xrightarrow{Ads.} O=\overset{(III)}{As}-O^- \xrightarrow{-1e^-} [O=\overset{(IV)}{As}-O^-] \xrightarrow[H_2O]{-1e^-} {}^-O-\overset{O^-}{\underset{O}{\overset{|\,(V)}{\underset{\|}{As}}}}-O^-$$

$$\mathbf{B}:\ pH \sim 7,9:\quad O=\overset{(III)}{As}-O^- \xrightarrow[H_2O]{-2e^-} {}^-O-\overset{O^-}{\underset{O}{\overset{|\,(V)}{\underset{\|}{As}}}}-O^-$$

Fig. 15.6 Proposed oxidation mechanism of arsenite at Pt surface at various pH values (Mohammad Abul et al. 2016)

reverse potentials with CV in 1 M HCl containing 10 μM As (III), e.g. –0.1 V, −0.2 V, −0.3 V, −0.4 V, −0.5 V and – 0.6 V (vs. SCE), respectively. It was observed that more negative potential can be used on gold nanoparticle modified ITO electrodes while the most negative potential used on normal gold electrodes is −0.3 V (vs. SCE). LOD (S/N = 3) was calculated to be 5 ± 0.2 ppb with deposition at −0.6 V for 60 s in 1 M HNO_3 by linear sweep voltammetry. Mohammad Abul et al. (2016) observed the kinetics of electrocatalytic oxidation of arsenite ions at a platinum electrode using cyclic voltammetry convolution potential sweep voltammetry and electrochemical impedance spectroscopy. The oxidation reaction of arsenite is observed at acidic, basic and neutral medium. At the basic medium, the oxidation process follows first-order kinetics, while in the acidic medium, the reaction order is fractional (Fig. 15.6). By analysing CV and CPSV data, it was suggested that at the Pt surface, a stepwise (As (III) → As (IV) → As (V)) process is involved in the

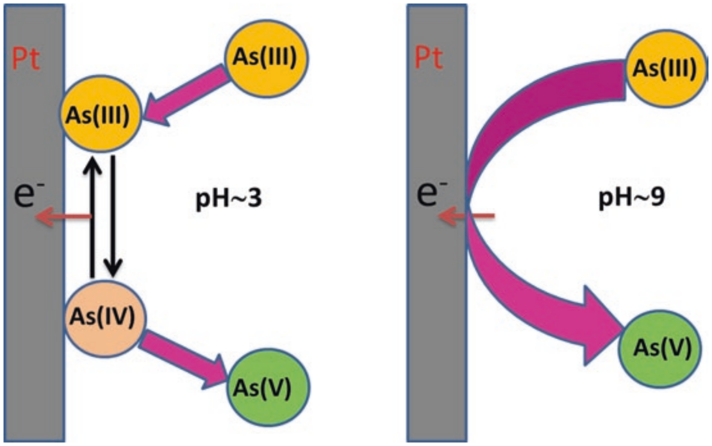


Fig. 15.7 Schematic diagram of electrooxidation of As^{3+} on Pt surface at variable pH (Mohammad Abul et al. 2016)

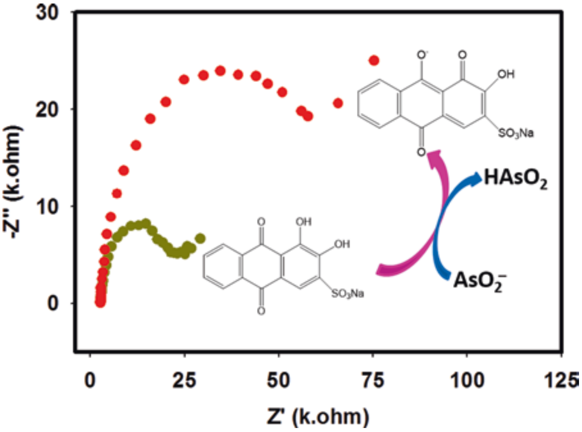


Fig. 15.8 Comparative EIS spectra of arsenic and arsenic + ARS in ITO electrode (Nahida et al. 2016)

acidic pH (e.g. 3–5); meanwhile, the mechanism is concerted in the neutral and basic medium. Based on CV and EIS data, it was suggested that different types of oxide species, on the platinum surface at different pH values, play roles to determine the reaction mechanism (Fig. 15.7) :

Tanjila et al. (Nahida et al. 2016) studied interferences of arsenite ions on electrocatalytic oxidation of alizarin red S (ARS) which was studied using Pt and ITO electrodes. A Pt electrode can oxidize both arsenite ions and ARS molecules simultaneously. The oxidation wave of ARS exceeds that of arsenite until the [AsO2^{-}]/[ARS] ratio surpasses 0.07. Meanwhile, an ITO electrode can oxidize only ARS molecules. It was seen that the diffusion coefficient of ARS molecules decreased from 4.3×10^{-6} cm^{-2} s^{-1} to 1.68×10^{-7} cm^{-2} s^{-1} in the presence of arsenite ions. The electrokinetic investigation shows that ARS oxidation was a two-electron transfer consecutive process. The EIS studies showed that charge transfer resistance was increased in the presence of arsenite ions during ARS oxidation (Fig. 15.8).

The ARS molecules are deprotonated in the presence of arsenite ions. The deprotonated form of ARS molecules involves increase of charge transfer resistance and decrease of diffusion coefficient (Fig. 15.8 and Table 15.1).

15.4 Electrochemical Detection of Arsenate (As^{5+})

Arsenic can be detected by atomic emission spectroscopy (Jitmanee et al. 2005), graphite furnace atomic absorption (Waeles et al. 2010) or atomic fluorescence spectroscopy (Cullen et al. 1994). Although such spectroscopic methods have good sensitivity and speciation capabilities, they are not readily used for in situ or onsite analysis. An alternative is to use voltammetry that is eminently portable, potentially enabling detection in the field (Gibbon-Walsh et al. 2012). As mentioned before that As(V) is less mobile than As(III). Because the movement of As(V) is retarded by its electrostatic attraction towards the positively charged particles, e.g. iron hydroxides

Table 15.1 Detection of arsenite by different electrodes

Electrode materials	Method	Deposition time/(s)	Limit of detection/ppb	Linear range/ppb	Supporting electrolyte
Platinum nanoparticle modified boron-doped diamond microelectrodes (Hrapovic et al. 2007b)	LSV,SWV		0.5	Up to 100	0.2 M potassium chloride
Gold nanoparticle/boron-doped diamond electrodes (Liza et al. 2008b)			30		0.1 M nitric acid
	ASV		1		0.1 M phosphate buffer (pH 7)
Iridium-implanted boron-doped diamond electrodes (Ivandini et al. 2006)	CV		1.5	0.1–100	0.1 M phosphate buffer(pH 4)
Gold nanoparticle modified ITO electrodes (DAI and Compton 2006b)	LSV	60	5 ± 0.2		0.05 M H_2SO_4
Platinum nanoparticle modified glassy carbon electrodes (Dai and Compton 2006a)	CV		2.1 ± 0.05	1–50	1 M $HClO_4$
Gold nanoparticle modified glassy carbon electrode (Majid et al. 2006)	SWASV	120	0.25	Up to 15	
Glassy carbon electrode modified with cobalt oxide nanoparticles (Abdollah et al. 2008)	CV		0.011	2–100	Buffer solution (pH 7)
Hanging mercury drop electrode (HMDE) (Pereir et al. 2007)	DPASV		0.5	2–80	2.0 M HCl + 3.15 × 10^{-4} M Cu (II)
Gold nanoparticle modified carbon nanotubes (Xiao et al. 2008)	ASV	120	0.1		0.1 M HCl

CV cyclic voltammetry, *ASV* anodic stripping voltammetry, *DPASV* differential pulse anodic stripping voltammetry, *SWV* square wave voltammetry, *SWASV* square wave anodic stripping voltammetry, *LSV* linear stripping voltammetry

(Domenico and Schwartz 1998b). So, As (V) become electrochemically inactive, and direct electrochemical detection is not possible in neutral pH. But many electrochemical detections have been performed by taking the advantages of chemical electrochemical (CE) or electrochemical-chemical-electrochemical (ECE) process (Forsberg et al. 1975; Barra and dos Santos 2001; Bodewig et al. 1982a; Hamilton et al. 1980; Yuh-Chang et al. 1997).

However, the direct determination of As (V) was found by the copolymer poly(aniline-co-o-aminophenol) (PANOA) that can strongly catalyse the reduction of arsenate in NaCl solution under cyclic voltammetric technique. The PANOA copolymer deposited on a glassy carbon (GC) electrode (3 mm diameter) was used for the detection of As (V). At the negative potentials, the emeraldine salt of PANOA is quickly reduced to leucoemeraldine and then arsenate was reduced by leucoemeraldine. It was found that the PANOA electrode can be used to determine directly As (V) concentration in a wide linear range (n = 19) of 0.949 and 495 μM with a correlation coefficient of 0.995 and a limit of detection of 0.495 μM. The sensitivity of the electrode was 0.192 $\mu A \mu M^{-1}\ cm^{-2}$. The response current increases with increasing pH from 4.5 to 6.0, a maximum response appears at pH 6.0, and then the response current decreases as the pH increases from 6.0 to 7.0. The nature of arsenate predominates over the effect of pH on the electrochemical activity of PANOA at pH < 6.0, in which arsenate exists in $H_2AsO_4^-$ form due to the fact that the dissociation constants of arsenic acid are $K_1 = 5.6 \times 10^{-3}$ and $K_2 = 1.7 \times 10^{-7}$ (Ya et al. 2009).

The determination of arsenate As (V) in neutral pH (=7) waters is considered impossible due to electroinactivity of As (V). However, the reduction of As (V) to As (III) was mediated by elemental Mn on the electrode surface in a novel redox couple in which two electrons are exchanged causing the Mn to be oxidized to Mn (II) in natural waters of neutral pH including seawater by ASV using a manganese-coated gold microwire electrode. The ECE reaction mechanism of the reduction of As (V) by Mn at the working electrode during the deposition step at −1.3 V is as follows:

$$\mathrm{Mn}(\mathrm{II}) + 2\mathrm{e}^- \rightarrow \mathrm{Mn}(0)(\text{electrochemical})$$

$$\mathrm{As}(\mathrm{V}) + \mathrm{Mn}(0) \rightarrow \mathrm{As}(\mathrm{III}) + \mathrm{Mn}(\mathrm{II})(\text{chemical})$$

$$\mathrm{As}(\mathrm{III}) + 3\mathrm{e}^- \rightarrow \mathrm{As}(0)(\text{electrochemical})$$

Elemental Mn is freshly produced on the electrode surface during deposition of adsorbed Mn (II) in underpotential conditions at potentials between −1.2 and − 1.4 V (Gibbon-Walsh et al. 2012) at pH 8. Mn is added to excess (~1 M Mn) to the water leading to a Mn coating during the deposition of As on the electrode at a deposition potential of −1.3 V. Deposition of As (0) from dissolved As (V) caused elemental Mn to be re-oxidized to Mn (II) in a 1:1 molar ratio providing evidence for the reaction mechanism. The detection limit was 0.2 nM As (V) using a deposition time of 180 s (Gibbon-Walsh et al. 2012). Sun et al. (2011) followed the reduction procedure of Bodewig (et al. 1982b) to reduce As (V) into As (III). Electroinactive As (V) was reduced to As (III) by gaseous SO_2 prior to ASV determination by using gold film electrode. For a deposition time of 4 min the determination limit was approximately 0.19 ppb. The sensitivity of gold film electrode was found quite unsatisfactory due to the interference of chloride ion. The chloride ion has a tendency for complex formation with gold (Frederick and Irving 1957; Delahay 1954). The possible mechanism of declining sensitivity was deduced as follows: the plated gold film was oxidized in the sample solutions (seawater + HCl) which contained high concentration of chloride ion to give the auric chloride ion complex ($AuCl_4^-$) (Delahay 1954). Thus, the active gold surface for the deposition of arsenic was reduced, and the reproducibility of the stripping peaks became disadvantageous. However, this problem was eliminated by establishing a 'make-up' procedure, i.e. the original active surface area was restored between each run through replating the electrode with gold solution containing no chloride ion. In addition, copper ion can also make interferences that give a strong combined oxidation peak near about 0.33 V (Kuwabara et al. 1973). In order to make up the gold film on the electrode and get rid of co-deposited copper simultaneously, 0.5 V potential was used as a make-up potential. Ferreira et al. (Ferreira and Barros 2002a) reported the determination of As (V) in natural waters by cathodic stripping voltammetry using a HMDE in presence of Cu (II). Cu (II) is used as it involves the preconcentration of a copper-arsenic intermetallic compound at the mercury electrode. Generally, the methods proposed for the determination of both As (III) and As (V) consist of the determination of the first species, followed by reduction of As (V) to As (III) and determination of total arsenic; As (V) is obtained by difference. The reduction of As (V) was performed with thiosulphate and the subsequent determination of the As (III) formed. This method has been shown to be reliable because the presence of the reductant is eliminated by using higher amount of copper ion. For determination of As (III), the quantification limit was 0.2 ppb for a deposition time of 40 s, and the relative standard deviation (RSD) was calculated to be 6% (n = 13) for a solution with 8 ppb of As (III). For As (total), the quantification limit was 2 ppb for a deposition time of 3 min, and the RSD was calculated to be 3% (n = 10) for a solution with 8 ppb of As (V). Günter et al. (1997) described a voltammetric stripping procedure for the determination of As (V) in a mannitol-sulphuric acid medium. They showed that the mannitol concentration must be 0.22 mol L^{-1} for high sensitivity. The additional advantage of the enhanced sensitivity by the use of mannitol is a reduction of the concentration of copper which must be added to the supporting electrolyte. However, maximum response was obtained when only 10 mg L^{-1} copper were added. The arsenic is co-precipitated with copper and selenium and reduced to arsine at the hanging mercury drop electrode. Using an accumulation time of 240 s, the detection limit is 0.52 μg L^{-1} and the determination limit is 0.9 μg L^{-1} (Table 15.2).

Table 15.2 Detection of arsenate by different electrodes

Electrode materials	Method	Deposition time/(s)	Limit of detection/ppb	Linearrange/ µM	Sensitivity / µA μM^{-1} cm^{-2}	Supporting electrolyte
Poly(aniline-co-o-aminophenol) electrode (Ya et al. 2009)	CV		0.495	0.949–495	0.192	0.10 M NaCl
Manganese-coatedgold microwire electrode (Gibbon-Walsh et al. 2012)	ASV	180	0.002			0.01 M HCl
Gold electrode (Gründler and Flechsig 1998)	ASV		0.056			HCl
Gold film glassy-carbon electrode (Kuwabara et al. 1973)	ASV	240	0.19			2 M HCl
Gold microwire electrode (Pascal et al. 2007)	SWASV	30	0.003			0.1 M HCl
Hanging mercury drop electrode (Greulach and Henze 1995)	CSV	60	4.4			2 M NaClO, 0.3 M NaCl, 0.5 M Mannitol
Hanging mercury drop electrode (Ferreira and Barros 2002b)	SWCSV	180	2			1 M HCl
Hanging mercury drop electrode (Günter et al. 1997)	CSV	240	0.52			Sulphuric acid, Mannitol, Cu(II), Se(IV)
Hanging mercury drop electrode (HMDE) (Pereir et al. 2007)	DPASV		0.5	2–80		2.0 M HCl + 3.15 × 10^{-4} M Cu(II)

CSV cathodic stripping voltammetry, *SWCSV* square wave cathodic stripping voltammetry

15.5 Conclusion

The most popular electrochemical methods for the determination of arsenic have been described in this chapter. Among different electrochemical methods, the stripping voltammetry is found very efficient and promising technique using Au electrodes or Au NPs on GC in HCl for analysis of As(III) in contaminated water samples. The method is particularly convenient to measure the most toxic As (III) at low ppb level in the presence of high concentration of As(V). Although As (V) is electroinactive, the direct determination of As(V) is found to be possible by the copolymer poly(aniline-co-o-aminophenol)-deposited GC electrode by cyclic voltammetric technique. Hanging mercury drop electrode is seen to be used frequently for the detection of As(V). Amperometric technique is followed for the determination of LOD.

Acknowledgements The authors acknowledge the Ministry of Education, Bangladesh and the World Academy of Sciences for the financial support and development of their laboratory facilities.

Conflict of Interest The authors didn't have any conflict of interest regarding this contribution.

References

Abdollah S, Michael EH, Craig EB, Richard GC (2004) https://doi.org/10.1039/B312285A

Abdollah S, Hussein M, Rahman H, Saied S (2008) Sensors Actuators B 129:246–254. https://doi.org/10.1016/j.snb.2007.08.017

Abedin MJ, Feldmann J, Meharg AA (2002) Plant Physiol 128(3). https://doi.org/10.1104/pp.010733

Akane S, Tribidasari A. I, Kenji Y, Akira F, Genko, Taizo N, Nobutaka H, Shigeru K and Yasuaki E. (2007) https://doi.org/10.1021/ac071519h

Andreae MO (1979) Limnol Oceanogr 24:440. https://doi.org/10.4319/lo.1979.24.3.0440

Baron R, Sljukic B, Salter C, Crossley A, Compton RG (2008) https://doi.org/10.1134/S003602440709018X

Barra CM, dos Santos MMC (2001) Electroanalysis 13:1098

Bauer C, Jacques P, Kalt A (2001) J Photochem Photobiol A Chem 140:87–92. https://doi.org/10.1016/S1010-6030(01)00391-4

Bodewig FG, Valenta P, Nurnberg HW (1982a) Fresenius' Z Anal Chem 311:187

Bodewig FG, Valenta P, Nürnberg HW (1982b) Z Anal Chem 311:187. https://doi.org/10.1007/BF00476644

Cabelka TD, Austin DS, Johnson DC (1984a) J Electrochem. https://doi.org/10.1149/1.2115916

Cabelka TD, Austin DS, Johnson DC (1984b) J Electrochem Soc. https://doi.org/10.1149/1.2115916

Cullen WR, Harrison LG, Li H, Hewitt G (1994) Appl Organomet Chem 8:313. https://doi.org/10.1002/aoc.590090703

Dai X, Compton RG (2006a) https://doi.org/10.1039/B513686E
Dai X, Compton RG (2006b) https://doi.org/10.2116/analsci.22.567
Dai X, Nekrassova O, Hyde ME, Compton RG (2004) https://doi.org/10.1021/ac049232x
Dai X, Nekrassova O, Hyde ME Compton RG (2004a) https://doi.org/10.1021/ac049232x
Dai X, Nekrassova O, Hyde ME, Compton RG (2004b) Anal Chem 76:5924. https://doi.org/10.1021/ac049232x
Davis PH, Dulude GR, Griffin RM, Matson WR, Zink EW (1978) https://doi.org/10.1021/ac50023a031
Delahay P (1954) New instrumental methods in electrochemistry. Inter Science Publishers, New York
Dhillon A, Nair M, Kumar D (2015) Anal Methods 7:10088–10108. https://doi.org/10.1039/C5AY02430G
Domenico P, Schwartz F (1998a) Physical and chemical hydrogeology, 2nd edn. John Wiley & Sons, Inc, New York
Domenico P, Schwartz F (1998b) Physical and chemical hydrogeology, 2nd edn. John Wiley & Sons, Inc, New York
Ferreira MA, Barros AA (2002a) Anal Chim Acta 459:151–159
Ferreira MA, Barros AA (2002b) Anal Chim Acta 459:151–159. https://doi.org/10.1016/S0003-2670(02)00086-7
Forsberg G, O'Laughlin JW, Megargle RG, Koirtyohann SR (1975) https://doi.org/10.1021/ac60359a057
Francesconi KA, Kuehnelt D (2004) Analyst 129:373–395. https://doi.org/10.1016/j.proche.2015.12.125
Frederick B, Irving S (1957) Anal Chem 29(2). https://doi.org/10.1021/ac60122a039
Gibbon-Walsh K, Salaün P, van den Berg MG (2012) https://doi.org/10.1016/j.aca.2011.10.041
Gregory BS, Torsten R, Burkhard R (2002) https://doi.org/10.1016/S0022-0728(02)00688-5
Greulach U, Henze G (1995) Anal Chim Acta 306:217–223. https://doi.org/10.1016/0003-2670(94)00681-B
Gründler P, Flechsig G-U (1998) Electrochim Acta 43(23):3451–3458. https://doi.org/10.1016/S0013-4686(98)00091-7
Günter H, Wolfram W, Sylvia S (1997) Anal Chim Acta 349:93–99. https://doi.org/10.1016/S0003-2670(96)00591-0
Hamilton TW, Ellis J, Florence TM (1980) https://doi.org/10.1016/S0003-2670(01)93621-9
Haruta M (2007) ChemPhysChem 8:1911
Hieda M, Garcia R, Dixon MC, Daniel T (2004) https://doi.org/10.1063/1.1643531
Holak W (1980) Anal Chem 52:2189. https://doi.org/10.1021/ac50063a044
Hrapovic S; Luong JHT (2003) https://doi.org/10.1021/ac026438u
Hrapovic S, Liu Y, Luong JHT (2007a) Anal Chem 79(2):500–507. https://doi.org/10.1021/ac061528a
Hrapovic S, Liu Y, Luong JHT. (2007b) https://doi.org/10.1021/ac061528a
Hung DQ, Nekrassova O, Compton RG (2004) https://doi.org/10.1016/j.talanta.2004.01.027
Innocenzo GC (2002) https://doi.org/10.1016/S0022-0728(02)00642-3
Ito K, Palmer CD, Steuerwald AJ, Parsons PJ (2010) J Anal At Spectrom 25:1334–1342. https://doi.org/10.1039/C001081B
Ivandini TA, Sato R, Makide Y, Fujishima A, Einaga Y (2006) https://doi.org/10.1021/ac0519514
Jafarian M, Mahjani MG, Heli H, Gobal F, Khajehsharifi H, Hamedi MH (2003) https://doi.org/10.1016/S0013-4686(03)00399-2
Jitmanee K, Oshima M, Motomizu S (2005) https://doi.org/10.1016/j.talanta.2004.09.024
Kao WH, Kuwana T (1985) J Electroanal Chem 193:145
Kaplin AA, Veits NA, Stromberg AG (1973) Z Anal Khim 28:2192
Kopanica M, Novotny L (2008) https://doi.org/10.1016/S0003-2670(98)00220-7

Korolczuk M, Ochab M, Rutyna I (2015) Talanta 144:517–521. https://doi.org/10.1016/j.talanta.2015.06.084

Kristien B, Jean-Michel F, Filip F, Wim L, Andrew C, Margit S, Gustaaf B, Bruno G, Paul D (2004) https://doi.org/10.1021/ac049893u

Kuwabara T, Suzuki S, Araki S (1973) Bull Chem Soc Jpn 46:1690

Li H, Smart RB (1996) Anal Chim Acta 325:25

Li Y, Song YY, Yang C, Xia XH (2007) https://doi.org/10.1016/j.elecom.2006.11.035

Liza R, Mika S, Robert W. F Richard G. C. Frank M (2008a). https://doi.org/10.1002/elan.200804226

Liza R, Mika S, Robert WF, Richard GC, Frank M (2008b) https://doi.org/10.1002/elan.200804226

Luong JHT, Lamb E, Male KB (2014a) Anal Methods 6:6157–6169. https://doi.org/10.1039/c4ay00817k

Luong JHT, Lam E, Male KB (2014b) Anal Methods 6:6157–6169. https://doi.org/10.1039/C4AY00817K

Majid E, Hrapovic S, Liu Y, Male KB, Luong JHT (2006) Anal Chem 78(3):762–769. https://doi.org/10.1021/ac0513562

Masanori F, Hisao Y, Shinji H, Naotoshi S, Yooshio T (2003) https://doi.org/10.1016/S0040-6090(03)00750-8

Mohammad Abul H, Mohammad Mahmudul H, Nahida T, Md Mahbubul A, Md Musfiqur R (2016) https://doi.org/10.1016/j.electacta.2016.12.055

Montilla F, Morallón E, Duo I, Comninellis C, Vázquez JL (2003) Chim Acta 48:3891

Moonis Ali K, Yuh S (2011) Asian J Chem 23(5):1889–1901

Myers DJ, Osteryoung J (1973) Anal Chem 45:267

Nahida T, Md. Asif R, Saiful A, Iqbal Ahmed S, Mohammad Abul H (2016) RSC Adv 6:93162–93168. https://doi.org/10.1039/C6RA21356A.

Pascal S, Britta Planer F, van den Berg CM (2007) Anal Chim Acta 585:312–322. https://doi.org/10.1016/j.aca.2006.12.048

Pereir M d SS, Winter E, Guimara JR, Rath S, Fostier AH (2007) Environ Chem Lett 5:137–141. https://doi.org/10.1007/s10311-007-0094-1

Rassaei L, SillanpOO M, Milsom EV, Zhang XH, Marken F (2008) https://doi.org/10.1007/s10008-007-0424-z

Rosemary F and Samuel P. Kounaves (2000) https://doi.org/10.1021/ac991185z

Sabahudin H, Yali L, Gary E, John HTL (2003) https://doi.org/10.1021/la0269199

Sadana RS (1983) Anal Chem 55:304

Schumacher S, Nagel T, Scheller FW, Eichelmann NG (2011) Electrochim Acta 56:6607–6611. https://doi.org/10.1007/s11581-017-2288-2

Shulga OV, Jefferson K, Khan AR, DFSouza VT, Liu JY, Demchenko AV, Stine KJ (2007) https://doi.org/10.1021/cm070238n

Siné G (2006) Thesis, EÄ colePolytechniqueFe’de’rale de Lausanne, Switzerland, pp 80–85

Sun F, Osseo-Asare KA, Chen Y, Dempsey BA (2011) J Hazard Mater 196:311–317. https://doi.org/10.1016/j.jhazmat.2011.09.029

Suna J, Lua H, Duc L, Lina H, Li H (2011) Appl Surf Sci 257:6667–6671

Takahashi Y, Sakamitsu M, Tanaka M (2011) Dyes Pigments 9:324–331

Tomilov AP, Smetanin AV, Chernykh IN, Smirnov MK (2001) Russ J Electrochem 37:1157

Trushina LF, Kaplin AA (1970) Z Anal Khim 25:1616

U.S. Environmental Protection Agency (1994) Integrated risk information system. (IRIS) on Arsine, Washington

U.S. Environmental Protection Agency (2007). Available from: www.epa.gov/safewater/arsenic.html1

Waeles M, Vandenhecke J, Cabon JY, Garnier C, Riso RD (2010) https://doi.org/10.1016/j.ecss.2010.09.003

Wang J, Swain GM, Tachibana T, Kobashi K (2000) J New Mater Electrochem Syst 3:75

Williams DG, Johnson DC (1992) https://doi.org/10.1021/ac00041a009

Wood DF, McKenna RH (1962) Analyst 87:880–883

World Health Organization (2004). Available from: www.WHO.int/watersanitationhealth/water-quality/arsenic.html

Xiao L, Wildgoose GG, Compton RG (2008) Anal Chim Acta 620:44–49. https://doi.org/10.1016/j.aca.2008.05.015

Ya Z, Qin L, Li S, Jianping Z (2009) J Electroanal Chem 636:47–52. https://doi.org/10.1016/j.jelechem.2009.09.009

Yi D, Mingwei C, and Jonah E. (2004) https://doi.org/10.1021/ja0320119

Yuh-Chang S, Jerzy M, Mo-Hsiung Yang (1997) DOI : https://doi.org/10.1016/S0039-9140(96)02197-2

Zaggout FR, Qarramam AEA, Zourab SM (2007) J Matter Lett 6:4192

Bio-nano Approaches: Green and Sustainable Treatment Technology for Textile Effluent Challenges

16

Priti Raj Pandit, Dinesh Kumar, Labdhi Pandya,
Raghawendra Kumar, Zarna Patel,
Shivarudrappa B. Bhairappanavar, and Jayashankar Das

Abstract

Globally, the textile industry is considered as a major contributor to the development of the country. However, the improper disposal of colored wastewater in the ecosystem leads to various environmental and health-related problems. Color removal, mainly from the textile wastewater effluent, has been the biggest challenge from the past decade. Various physiochemical, biotechnological, and nanotechnology methods have been used to overcome these challenges. However, no such method has been reported for effective and economical treatment for textile wastewater. Effluent from textile processes such as dyeing, manufacturing, and finishing processes contains a high concentration of chemicals, including acids, binders, salts, etc., which are hazardous to environment and ecosystem. Furthermore, various chemicals used for the sizing, softening, and brightening of the fabric are also present in the wastewater. Therefore, textile wastewater effluent needs an eco-friendly and economically viable method for effective treatment. This book chapter provides a critical review on the advancement in treatment technologies available for decolorization, degradation, and mineralization of the textile wastewater and also suggested an effective and economically viable alternative for textile effluent.

Keywords

Biotechnological · Nanotechnology · Mineralization · Azo dyes · Textile effluent

---

P. R. Pandit · D. Kumar · L. Pandya · R. Kumar · Z. Patel · S. B. Bhairappanavar · J. Das (✉)
Department of Science and Technology (DST), Gujarat Biotechnology Research Centre (GBRC), Gandhinagar, Gujarat, India

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_16

16.1 Introduction

The environmental problems and toxic pollutants produced by industrial processes are one of the major challenges faced worldwide. Among the industries, the textile industry has been increasing consistently with a significant contribution to global development. However, textile manufacturing yields a large amount of colored and highly toxic wastewater, which leads to hazardous effects on the environment (Jilani 2015). The usage of synthetic dye has been increased subsequently in the textile and dyeing industry due to their cost-effectiveness, high stability to light, temperature, detergent, and microbial attack as compared to natural dye (El-kassas 2014). Almost 10,000 different synthetic dyes are currently manufactured mainly azo dyes and are frequently used by the textile and various other industries for dyeing due to more economical stability than natural dyes (Xu et al. 2007b). Azo dyes are the largest class of synthetic dye, which are characterized by the presence of azo (-N=N-) groups in their structure. These dyes are toxic and highly persistent to the environment, and their metabolic products are mutagenic and carcinogenic in nature (Xu et al. 2007a). The presence of these toxic and carcinogenic products leads to the serious environmental pollution. A large amount of these textile dyes and pigments are lost during the finishing process and discharged as industrial effluents at various stages. The presence of azo and vat dyes, sodium silicates, formaldehyde-based dye fixing agents, softeners and non-biodegradable agents, soaps and detergents, and heavy metals is a continuous threat to all living beings. It is reported that nearly 10–15% of these dyes are directly discharged into open water bodies, such as rivers and lakes during the manufacturing process (Mani and Bharagava 2018).

In India, due to high demand for cotton and polyester, the textile industries consume around 80% of the total production of 1,30,000 tons of dyestuff. These dyes in wastewater affect aquatic life due to the occurrence of toxic metal components. Presently, heterocyclic and aromatic are widely used by the textile industry. The complex and stable structure of dye is poising a greater difficulty in degrading the textile wastewater but also in any kind of complex matrix (Holkar et al. 2016). The use of synthetic dyes has tremendously increased in the textile processes, and its exposure to human has led to health concerns and serious ecological consequences. Therefore, there is an urgent need for treatment of textile effluent before being discharged to the open environment.

The treatment of textile effluent involves physical, chemical, and biological methods such as coagulation, adsorption, filtration, and using chemical flocculates. However, many technologies have been developed by the scientific community such as bioremediation of azo dye using bacteria, fungi, and plant extract (Lavanya 2014). Moreover, the enzymatic remediation of azo dye seems to be the most promising remediation method. However, isolation and characterization of the various potential enzymes for azo dye degradation is a time-consuming and expensive process. To overcome the disadvantage of chemical and physical methods, the researchers have focused on the development of the nanoparticles. Nanotechnology is the alternative to the conventional physicochemical approaches as it is clean and eco-friendly to the environment (Khatoon N and Sardar M 2017).

The aim of this chapter is to provide an overview of the different wet processing steps in the textile industry. This chapter also explains the current treatment technologies for degradation of the textile wastewater.

16.2 Processing Steps in the Textile Industry

The manufacturing steps in textile industries involve different processes from the processing of the raw material to the final product development. It starts in collecting and arranging the fibers, then transforming fibers into yarn, and altering the yarn into fabric, and then this fabric goes into various wet processing steps. The major steps involved in the manufacturing process of textile industries include yarn formation, fabric formation, fabric/wet processing, and textile fabrication (Madhav et al. 2018). The wet processing steps of textile fabrics are described in details as follows (Fig. 16.1):

16.2.1 Sizing

In this process, the protruding loose fibers are removed by the action of heat or direct flame. The sizing agents are selected based on the type of textile material, cost-efficacy, etc. This step utilizes the cellulosic- and protein-based starch derivatives such as methylcellulose and oxyethlycellulose, glue, and gelatin as sizing agents for the initial texture smoothing of the textile material. Moreover, carboxymethylcellulose (CMC) and polyvinyl alcohol (PVA) are widely used as a secondary sizing agent for cotton yarns (Madhav et al. 2018). The other similar synthetic anionic groups such as modified polyesters, glycols, sulfonic acids, and polyurethane anionomer are used in the sizing of the textile industries (Regan 1962).

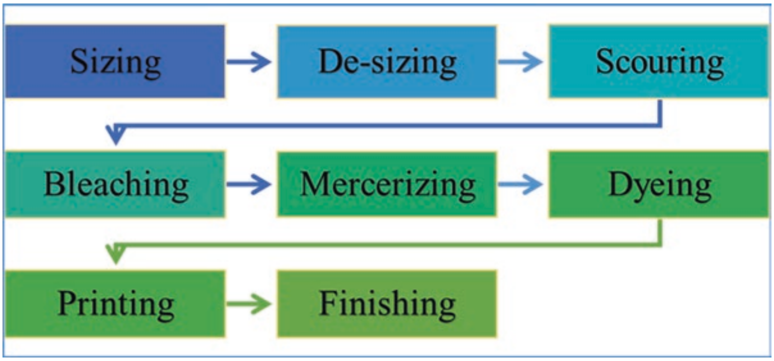


Fig. 16.1 Workflow and concept of major processing steps involved in textile industry

16.2.2 De-sizing

In the de-sizing process, the threads are attached together, preventing them from breakages in the loom, where the warps are strengthened with mechanical stresses and friction with the help of de-sizing agents (Regan 1962). The de-sizing agents are originally enzymes produced from syrup extracts such as *amylase*, *maltase*, *cellulose*, etc. The enzymatic-based de-sizing agents are widely used in wet textile processing because it produced little wastewater and is eco-friendly to fabric texture (Chatha et al. 2017).

16.2.3 Scouring

The term scouring in textile industry implies removing the impurities without causing damage to the fabric. The impurity includes dirt, surfactants, soaps, fats, gums, pectin, oils, and waxes along with nonfibrous impurities. In this process, both natural and added impurities are removed with hydrophobic functionalities as completely as possible. In textile processing, consumption of extensive alkaline-based treatment leads to formation of various by-products in the wastewater effluent and poses severe damage to cellulose content of the fabric (Chatha et al. 2017). To overcome such problems, a wide range of industrially relevant enzyme such as cellulases, pectinase, proteases, and lipases along with the mix of the consortium has been investigated (Tzanov et al. 2001).

16.2.4 Bleaching

The purpose of the bleaching of the textile fibers is to remove the remaining stains and attached sizing, de-sizing, or scouring agents used in the previous steps and increase the dyeing efficiency of the textiles. The widely used bleaching agents in the textile industry include oxidizing agents such as H_2O_2, O_3, $Ca(OCl)Cl$, $Ca(OCl)_2$, NaOCl, $K_2Cr_2O_7$, etc. and reducing agents such as $FeSO_4$, H_2S, Na_2SO_4, $NaHSO_4$, etc. Among various bleaching agents, the hypochlorite, hydrogen peroxide, oxalic acid, and sodium silicate are widely used (Tanapongpipat et al. 2008).

16.2.5 Mercerizing

After the bleaching process, the mercerizing in textile industry is utilized to improve the tensile strength, durability, luster, and dyeing efficiency of the fabrics. In the mercerizing process, the cotton fabric is treated with a high concentration (about 18–24% by weight) of sodium hydroxide. After that, the fabric goes through the longitudinal shrinkage during impregnation in the sodium hydroxide solution. The most commonly used mercerizing agents for the cotton fiber are caustic soda and sodium hydroxide, which change the crystalline nature of the cellulose and cotton fibers (Ghosh et al. 2004; Duchemin et al. 2012). The excessive mercerizing agent is removed by washing 1–3 min while holding the cotton fabric under stress.

16.2.6 Dyeing and Printing

Dyeing is the process in which the fabric or yarn is treated with a dye to impart color. The auxochrome groups such as amine, carboxyl, sulphonate, hydroxyl, and chromophore groups like azo, carbonyl, nitro, quinoid groups in the dye are responsible for the color (Waring and Hallas 2013). There are several types of dyeing agents such as direct dyes, acid dyes, basic dyes, mordant dyes, and vat dyes for dyeing different kinds of fibers, etc. The different synthetic dyes have their own affinity toward a particular type of fiber (Rippon and Evans 2012). These dyes are also responsible for water pollution by rendering unacceptable color in the textile wastewater.

The process of printing is similar to dyeing, except in a way that printing is intended to impart color to the specific area of the textile material in the form of solution, while in dying, dye is applied in the form of thick paste to prevent its spread. The printing process also generates wastewater similar to dyeing effluent (Holkar et al. 2016; Manekar et al. 2014).

16.2.7 Finishing

In this process, fabrics are exposed to several types of finishing process like washing, drying, pressing, and conditioning. Specific properties such as softening, waterproofing, antibacterial, and UV protective are imparted to the fabric during the finishing process (C.R. Holkar et al. 2016). The list of pollutant compounds that are produced at different stages of wet processing is shown in Table 16.1.

16.3 Current Treatment Technology

16.3.1 Bio-based Technologies for Degradation and Mineralization

Recent decades have witnessed several physical- and chemical-based methods, which have been used for the decolorization of azo dye (Fig. 16.1). But these methods are costly, producing a huge amount of sludge after the treatment and required safe disposal (Uday et al. 2016: Liu et al. 2019). Physical method for the treatment such as adsorption and membrane filtration of textile effluent needs further treatment, so it has also been a time-consuming process (Uday et al. 2016). Apart from the recent development, biological treatment methods are most appropriate for degradation of effluent and also cost-effective and eco-friendly in nature (Song et al. 2003: Chen 2006). Most of the bio-based bioremediation is usually done by the use of microorganisms (algae, fungus, and bacteria) to remove the dye contained from the effluent. In this approach, microorganisms have the ability to adapt themselves in toxic wastes or dye

Table 16.1 List of compounds released during the processing steps in the textile industry

S. No	Processing step	Waste compounds in wastewater	Reference
1	Sizing	Polyvinyl acrylic (PVA) and acrylic resins, waxes	Choo et al. (2007)
2	De-sizing	Sodium bromide and sodium chlorite, high BOD, volatile organic compounds, glycol ethers	Harane et al. (2017)
3	Scouring	NaOH, detergents, fats, oils, wax, spent solvents, surfactants, alkyl phenol ethoxylates, alkyl benzene sulfonates	Sarayu and Sandhya (2010)
4	Bleaching	Hydrogen peroxide, sodium silicate and organic stabilize, alkaline pH, hypochlorite, peracetic acid, halogenated compounds	Rott and Minke (1999)
5	Mercerizing	High pH, NaOH, $ZnCl_{2,}$ cyclohexanols	Correia et al. (1994)
6	Dyeing	Metal salt, surfactants, toxics, organic processing assistance, cationic materials, color, BOD, sulfides, spent solvents, chromophores and auxochromes, NaCl	Babu et al. (2007)
7	Printing	Color, metal salts, formaldehyde, suspended solids, urea, hydrocarbons, solvents, BOD	Holkar et al. (2016)
8	Finishing	Softeners, resins, waxes, BOD, COD, suspended solids, spent solvents, formaldehyde-based cross-linking agents	Ghaly et al. (2014)

effluent and develop naturally new resistant strain (Saratale et al. 2011). However, such strain effective for the dye removal transforms toxic dye/chemicals to less toxic or harmful. The treatment of dye has several advantages and disadvantages with different treatment methods and a wide range of applicability (Fig. 16.2).

16.3.1.1 Microalgae-Based Biodegradation of Textile Effluent

Treatment of textile effluent using microalgae is the most important and effective process. Bio-based treatment process using the microalgae has potential to biotransforming, biodegrading, and adsorbing the dye which is present in natural wastewater (Aragaw and Asmare 2018). However, the rate of degradation was higher when using the microalgae compared to bacteria and fungus and subsequently eliminates the pollution in particulate wastewater (Aragaw and Asmare 2018). In most of the cases, green microalgae were used for the treatment of dye effluent, and such algae are present in freshwater and saltwater ecosystem (Gupta et al. 2014; Devi et al. 2016). Algae grown on the surface of waste water have large surface area which leads to high biosorption potential. Hence, the electrostatic force of attraction towards contamination present in wastewater is high. Several reports about harmful metabolites present in the wastewater such as PO_4^3, $RCOO^-$, $-NH^2$, and –OH are absorbed by the algae present in the wastewater surface (Al-Fawwaz and Abdullah 2016).

Mechanism of decolorization of the dye by algae is different as compared to fungus or bacteria. In the first stage, the algae biomass is converted into carbon dioxide and water. Second stage algae participate in the conversion of chromophore material to the nonchromophore material; after that final stage, chromophore is adsorbed by the algal biomass (Alvarez et al. 2015). Many studies have been reported (Table 16.2) showing the effective use of the algae against azo dye degradation by producing the

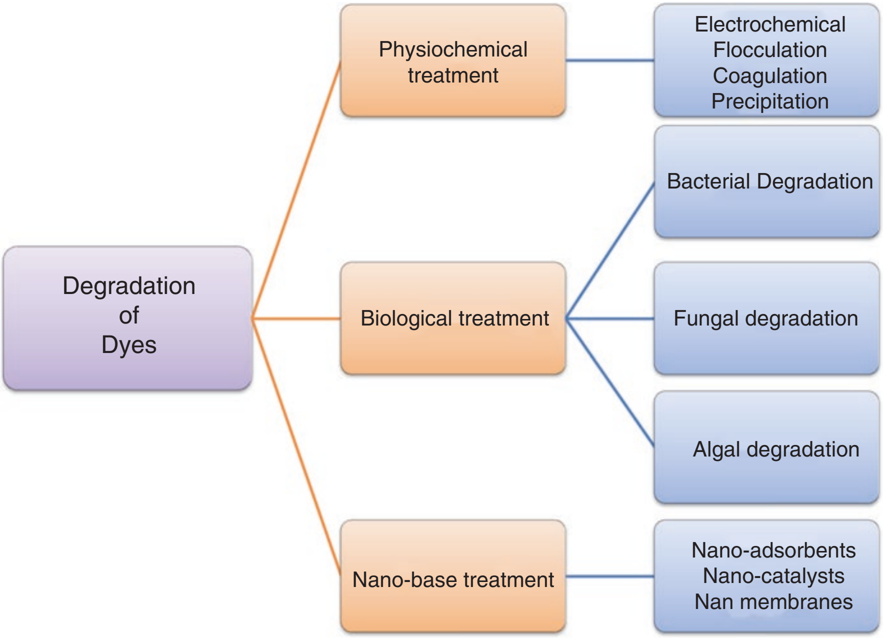


Fig. 16.2 Flow chart showing different methods for degradation of dyes

azoreductase enzyme for decolorization. Other studies have reported that algae species utilize azo dyes as C and N source for their growth.

16.3.1.2 Fungal-Based Biodegradation of Textile Effluent

Fungus-based biological methods for the treatment of dye were widely studied in white-rot fungus; such organism has the ability to degrade plant lignin and other polymers found in the plant cell wall (Bar and Aust 1994). However, not only white-rot fungus participates in decolorization of textile effluent, there are also different fungus strains reported which can decolorize or biosorb various dye or dye effluents (Przystas et al. 2015). According to the mode of action and surrounding environment, fungus can be classified in two types: live cell, which can either decolorize or biosorb the dye, and the dead cell (fungus biomass), which only adsorbs the dye. Several studies of different fungal strains and fungal-based degradations of dye have been reported for treating the wastewater discharge, and these studies successfully replace the physical- and chemical-based treatment methods (Table 16.3) (Lade et al. 2015a).

The biodegradation or bioremediation of effluent from textile, pulp, and paper industries is mainly carried out by using fungus. They are producing extracellular lignin-modifying enzymes, such as lignin peroxidase (Lip), manganese peroxidase (MnP), and laccase (Singh and Singh 2010). However, the participation of theses enzymes for degradation is different from each fungus (Lade et al. 2015b). For bioremediation, as compared to bacteria, different fungal cultures were used due a large amount of biomass, hyphal spectra and filamentous fungi are successfully degrade under certain niches due to large surface area and cell to cell communication (Singh et al. 2012; Joutey et al. 2013).

Table 16.2 Algae use for the decolorization of different dyes

Name of algae	Textile dyes	% of Degradation	Time of degradation	References
Desmodesmus sp.	Methylene blue (MB) Malachite green (MG)	64.4–98.4% 88.90%	4–6 days 4 days	Al-Fawwaz and Abdullah (2016)
Spirogyra rhizopus	Acid red 247	pH dependent	Variation pH range	Ozer et al. (2006)
Cosmarium sp. (2007)	Triphenylmethane Malachite green	Dye 63–74%	7 hrs	Daneshvar et al. (2007)
Synechocystis sp.	Reactive red	25.7%	20 days	Karacakaya et al. (2009)
Pithophora sp.	Malachite green	75–85%	2–3 hrs	Kumar et al. (2005)
Cystoseira barbatala	Methylene blue	Adsorption		Caparkaya and Cavas (2008)
Caulerpa lentillifera	Astrazon red Methylene blue RGB-red dye	Adsorption		Marungrueng and Pavasant (2007)
Nostoc muscorum (blue-green algae)	Methylene blue	96%		Sinha et al. (2015)
Ulva lactuca sargassum	Methylene blue	Adsorption		Tahir et al. (2008)
Caulerpa racemosa	Acid blue 9	Adsorption		Cengiz and Cavas (2008)

Table 16.3 Decolorization of textile effluent by fungal strain

Fungus	Dye	% of degradation	Reference
Phanerochaete chrysosporium	Effluent of textile and paper and pulp industries	20–100%	Senthilkumar et al. (2014)
Trichoderma Harzianum	Textile industry	43%	Singh and Singh et al. (2010)
Aspergillus oryzae	Biosorption of azo dyes	80%	Chairin et al. (2013)
Trametes polyzona strain WR710–1	Anthraquinone dye (reactive blue 4)	80%	Chairin et al. (2013)
Penicillium sp.	Wattle extract and various synthetic dyes	78%	Kanagaraj and Mandal (2012)
Aspergillus Niger	Wattle extract and various synthetic dyes	71%	Kanagaraj and Mandal (2012)

16.3.1.3 Bacterial-Based Biodegradation of Textile Effluent

The microbial population is already present in the dye effluent or wastewater due to complex feed substance in the wastewater and transforms them into the simplest form, improving treatment process. The treatment of wastewater is a common and reliable technique these days. Several reports already related to treatments of textile effluent, and a large number of numerous bacterial species participate in the degradation of dye and complex mineralization of different sorts of dyes. The huge advantages of such a process are low running costs, nontoxic end products, and being inexpensive. The process of degradation may be aerobic, anaerobic, and combination of both; most of the bacterial species are using the aerobic process for the treatment of dyes. Different types of dyes are degraded by several bacteria, but not all dye degradation by bacteria have been identified. In the framework of bioremediation, several reports have been conducted on numerous assessments on microorganism having the ability to catabolize organic pollutants.

Microorganisms are playing an important role in remediating several organic contaminates which can be used as pollution indicators for different toxic compounds (Everts and Kanwar 1994; Hruby et al. 2016). Using the bacterial culture for degradation is of main advantage as they can grow in a short period of time compared to other microorganisms. The manipulation of genes at genetic level can enhance the dye degradation ability of bacteria. The microorganisms present in the organic pollutants are able to catabolize chlorinated and aromatic hydrocarbon as an energy sources and can be used in the degradation of sulfur-based textile dyes (Yang et al. 2014; Nguyen et al. 2016). Different studies and identification of bacteria show how azo dyes are degraded in a short period of time. Several bacterial enzymes have been reported which participate in the breakdown of the azo bonds under both aerobic and anaerobic conditions (Wang et al. 2017). The intermediate metabolite products of dye should further be catabolized by other bacterial enzymes such as hydroxylase and oxygenase (Elisangela et al. 2009). The microbial consortium is widely used for the degradation of textile effluent due to its combined action of several enzymes. Table 16.4 showed the various bacterial strains and different dyes

Table 16.4 Decolorization of textile effluent by bacterial strain

Bacterial strain	Textile dyes	% of degradation	References
Bacillus endophyticus VITABR13	Acid red 128	90%	Prasad and Rao. (2011)
Shewanella sp. Strain IFN4	Reactive black 5, direct red 81, acid Red 88	90%	Imran et al. (2014)
Ganoderma lucidum *Coriolus versicolor*	Foron yellow RD5GL, Foron red RDRBLS, ForonRubine RDGFL, Foron Black RD3GRN, Foron blue RDGLN, Foron turquoise SBLN	93–98%	Sadaf et al. (2013)
Bacillus subtilis	Crystal violet	82%	Kochher and Kumar (2011)
Enterococcus sp. and *Klebsiella* sp.	Reactive blue 19; Dark green dye	95%	Gulati and Jha (2014)
Pseudomonas aeruginosa, *Clostridium perfringens*, *Proteus vulgaris*	Crystal violet	85% 94%	Ali and Akthar (2014)
Proteus sp. *Klebsiella* sp.	Light red dye	80.00%	Sethi et al. (2012)

(continued)

Table 16.4 (continued)

Bacterial strain	Textile dyes	% of degradation	References
Rhodococcus rhodochrous	Toluidine red	99.5%	Shah (2014)
Pseudomonas putida, *Klebsiella ozaenae*	Congo red (Direct red 28), Direct blue 80	90.67% and 97.2% 97.62% and 95.1%	Shinkafi et al. (2015)
Enterobacter sp. strain VP-64	Crystal violet	50%	Hemapriya and Vijayanand (2014)
Paenibacillus alvei MTCC 10625	Black WNN	95.1%	Pokharia and Ahluwalia (2016)
Pseudomonas aeruginosa, *Pseudomonas putida*	C.I. acid blue 113 (AB-113), C.I. Basic Red 46 (BR- 46), C.I. Direct blue 151 (DB-151), C.I. Direct Brown 2 (DB-2) A mixture of four dyes		Falavarjani et al. (2012)
Bacillus sp. *Aeromonas hydrophila* sp.	Provisional pink	93%, 85%	Celia and Suruthi (2016)
Bacillus pumilus	Congo red	96.99%	Modi et al. (2015)
Actinomyces sp. (PK07), *Pseudomonas* sp. (PK18), *Stenotrophomonas* sp. (PK23), Staphylococcus sp. (PK28)	Indigo dye	7% 92% 99% 86%	Rajendran et al. (2015)
Burkholderia sp.	Alizarin	89%	Sharma and Sharma (2015)
Bacillus sp. SG2	Drimarene red	85–90%	Oak et al. (2016)
Bacillus sp.	Methyl red Navy blue	86% 68.3%	Ezhilarasu (2016)
Providencia rettgeri strain HSL1	Reactive blue 172	99%	Lade et al. (2015a, b)
Pseudomonas aeruginosa *Ochrobactrum* sp.	Remazol blue	12.5% 89.4%	Kiliç and Dönmez (2012)

used for the degradation and few strains capable of decolorizing various types of dye which are structurally different.

16.3.1.4 Degradation Based on Biosorption

Biosorption is also effective using a full process where the biologically active material metabolites are participating in the absorption of textile dyes. Several researches have reported different bacterial species for the treatment of textile effluent which participate in the degradation of dye (Joshi et al. 2019). In the past few years, few reports were available, and researchers tried to use agricultural waste material such as wheat straw, cotton, leaves of pine trees, sugarcane bagasse, shells of cashew nut, fungal and yeast cells, bacterial biomass, and algal biomass (Robinson et al. 2002;

Tunc et al. 2009; Deniz and Karaman 2011; Kalaiarasi et al. 2012; Khataee et al. 2013; Ferreira et al. 2015). Using such process is cost-effective and minimal steps are required for processing (Vitorand Corso 2008). The limitation of biosorption process is because of the presence of heteropolysaccharide and lipid segments of the cell wall in the microorganism, which interfere with the adsorption process. The viability of biosorption depends upon several biotic and abiotic factors such as pH, temperature, ionic quality, contact time, concentration of dye, adsorbent dose, and structure of dye is much more important due to adherence in the microbial surface and type of microorganism (Deniz and Karaman 2011).

16.3.2 Nanotechnology-Based Approach

The nanotechnology is a branch of science which deals with the control, integration, and manipulation of various atoms and molecules at the nanoscale to form different materials (Homyak et al. 2008). Nanotechnology opens a new platform to treat wastewater more efficiently due to its higher surface-area-to-volume ratio, high absorption, interaction, and reaction capabilities (Kumar et al. 2017). The removal of hazardous compounds from wastewater with the help of nanomaterials is an eco-friendly and cost-effective technique. The nanomaterials are a small particle with few nanometers and synthesized in different forms such as nanowires, nanotubes, films, quantum dots, and colloids (Raman and Kanmani 2016). Based on the nature of nanomaterials, it may be classified into three main types: nanoadsorbents, nano-catalyst, and nanomembranes (Anjum et al. 2016).

16.3.2.1 Nanoadsorbents

Nanoadsorbents are nanoscale particles synthesized from organic or inorganic materials which have higher affinity towards adsorbing elements. Sorption is a process in which a material referred to as "sorbate" gets adsorbed on another substance, called sorbent, by physical or chemical interaction (Kumar et al. 2017). Sorbents are widely used for the removal of organic pollutants generated from textile effluent. The steps involved in sorption process is presented in (Fig. 16.3) (Kumar et al. 2017).

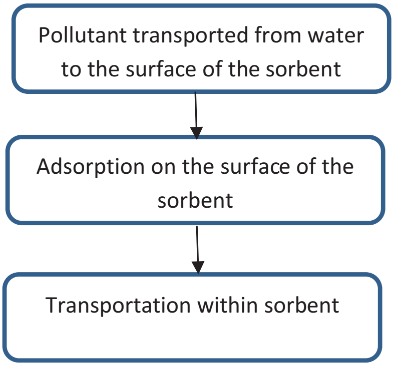


Fig. 16.3 Steps involved in the sorption process

Nanoparticles possess higher specific surface areas than the bulk particles. They have the ability to functionalize with different chemical groups and thus improves their affinity towards the target contaminants. These two properties make them very effective as sorbents. Moreover, nanosorbents possess nanosized pores which aids in the sorption of contaminants. The reversible nature of adsorbents can be regenerated by suitable desorption processes for multiple uses with a low maintenance cost, high efficiency, and ease of operation (Kumar et al. 2017). Therefore, the adsorption process has emerged as one of the major techniques for removal of pollutants from wastewater (Hua et al. 2012). Some of the nanosorbents are listed below:

Carbon Nanosorbents Carbon-based nanomaterials are well-known for the adsorption of various organic and inorganic pollutants in wastewater due to its non-toxicity and high sorption capacities. Primarily, activated carbon is used as sorbents, but it is difficult to remove organic and inorganic contaminants and heavy metals at parts per billion (ppb) levels. With the development of nanotechnology carbon nanotubes (CNTs), fullerene and graphene are synthesized and used as nanosorbents (Khajeh et al. 2013). The structure of CNTs, at the atomic scale is well-defined and uniform which makes them different from activated carbons (ACs). In ACs the parameters like pore diameter and adsorption energy are needed to quantify the adsorption whereas,in CNTs, one can deal directly with well-defined adsorption sites present on the adsorbed molecules (Kumar et al. 2017).

Carbon Nanotubes Carbon nanotubes (CNTs) are used for the removal of dyes and its intermediates coming from textile industry effluent. Active sites of the CNT surface play an important role in dye adsorption on CNTs. Their thermal, mechanical, electrical, and physical properties make them ideal for work on single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT). The main mechanisms of absorbing different dye compounds by CNTs depend on nature of the dyes that is cationic or anionic (Rajabi et al. 2017). The surface area to volume ratio of CNTs is greater than other common adsorbents which makes them more effective as compared to other commonly available adsorbents. The high contact surface ensures effective collisions between the molecules of the dyes and the surface of the carbon nanotubes, which in turn leads to an improvement in the efficiency of the adsorbent (Machado et al. 2012). Adsorption capacities of dye on CNTs can be enhanced by modifying CNTs with a functional group. Adsorption rate is further dependent on various other factors like pH, temperature, contact time, and initial concentration. For adsorption of cationic dye, high value of pH is favorable, and for anionic dye low value of pH is preferred (Machado et al. 2012). CNTs are also effective in removing polycyclic aromatic compounds (Hayati et al. 2011) and hence find special application in the textile industry as the dyeing process releases the maximum amount of aromatic compounds into the effluent stream. Activated carbon fibers synthesised by electrospinning of CNTs, which are nanoporous in nature showed increased affinity towards the organic sorption for benzene, toluene, xylene, and ethylbenzene (which are used as solvents in the textile industry) than granular activated carbon (Abou et al. 2015).

16.3.2.2 Metal Oxide Nanosorbents

Nanosized metal oxides are gaining attention for removal of heavy metals from textile wastewater compared to other conventional techniques like precipitation, ion exchange, and membrane filtration because of their fast kinetics, high activities, large surface areas, adsorption capacity, and selectivity. Some of the nanosorbents are used for wastewater treatment such as iron oxide, aluminum oxide, titanium oxide, manganese oxide, zinc oxide. Nano CuO adsorbent has been studied for removal of heavy metal ions such as Cd^{2+} and Fe^{3+} from wastewater by the adsorption mechanism (Taman et al. 2015). Removal of several organic pollutants present in wastewater using Fe oxide nanosorbents has been studied. The Fe oxides exhibit excellent adsorption capacity for heavy metal ions due to magnetic properties (Kumar et al. 2017). Hua et al. (2012) reported that titanium oxide (TiO_2) nanoparticles were able to remove multiple metals (Zn, Cd, Pb, Ni, Cu) from effluent. Studies reveal that removal of various heavy metal ions from wastewaters using nano alumina coated with sodium dodecyl sulfate on which 2,4-dinitrophenylhydrazine was immobilized found that the resultant adsorbent possesses high adsorption capacity for Cd^{2+}, Cr^{3+}, and Pb^{2+} (Afkhami et al. 2010). Nano-aluminum oxyhydroxides are considered and applied for the extraction of methyl violet from wastewaters and found to be successful (Kerebo et al. 2016). Iron oxide-alumina mixed nanocomposite fiber was prepared by means of electrospinning method, and its sorption nature was studied toward Cu^{2+}, Pb^{2+}, Ni^{2+}, and Hg^{2+}; the percentage removal was found to be in order $Hg^{2+} > Ni^{2+} > Pb^{2+} > Cu^{2+}$ with adsorption capacities (Mahapatra et al. 2013). Manganese oxide (MnOs) nanoparticle is widely used for the removal of various heavy metals such as arsenic from wastewater. Adsorption of various heavy metals such as Pb^{2+}, Cd^{2+}, and Zn^{2+} on HMOs usually happens due to the inner-sphere formation mechanism (Anjum et al. 2016). Zinc oxide (ZnO) can absorb heavy metals due to their porous micro-nanostructure with the high surface area. ZnO are widely used as nanoadsorbent for the removal of Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, and As^{3+} heavy metals from wastewater in the form of nano-paltes, nano-assemblies and nanosheets. Microporous nano-assemblies show high affinity towards the adsorption of mercury, lead and arsenic due to their electropositive nature (Gupta et al. 2015).

Zeolites Zeolite is an effective and economical option for the removal of basic dye from textile wastewater because of its low cost, high surface area, and high ion-exchange capability. More than 40 different types of zeolites occur in nature (Kumar et al. 2017). The higher adsorption capacity of zeolite is due to high porosity (Chunfeng et al. 2009). Linoptilolite natural zeolite is readily available in nature, and it is commonly used as adsorbent (Kandisa et al. 2016). MCM-22 is a novel nanoporous zeolite as it holds unusual framework topology, high thermal stability, large surface area, and good adsorption capacity, rendering this zeolite very interesting for adsorption and catalysis. It has been proved as an effective adsorbent to remove some basic dyes like methylene blue, crystal violet, and rhodamine B from aqueous solution (Wang et al. 2006). For removing of heavy metals, two natural zeolites were pre-treated with NaOH; it was found that the modified zeolites have high adsorption capacity for lead (Pb) and cadmium (Cd) with a metal removal efficiency of more than 99%.

Dendrimers Dendrimers are a class of macromolecules classified by a highly branched structure of great regularity with compact shape, and a large number of (reactive) end groups and spaces between the branches for taking up target molecules. Modified dendrimers have been applied to extract dyes either in liquid-liquid systems or liquid-solid systems (B. Hayati et al. 2011). Polyamidoamine (PAMAM) are polymer dendrimers synthesized from a monomer of ethylenediamine. Large internal cavities, high solubility, low viscosity, and the diversification of structure design are key features of PAMAM dendrimers. The surface of PAMAM dendrimer has –NH2 groups which entrap the contaminants and get adsorbed in its internal cavities which makes them prominent feature for degradation of dyes (Zhou et al. 2013). Three-dimensional PAMAM dendrimer-based polymeric network has been applied for extraction of azo dye (extraction of methyl orange dye) from aqueous solution (Ghosh 2008). Taleb et al. (2015) studied the adsorption of Isma acid fast yellow G dye using PAMAM/copper sulfide (CuS)/AA nanocomposite to determine the dye sorption character. The kinetics data indicates that the adsorption of dye was followed by pseudo-second-order kinetics with dye dosage of 25 and 100 mg/L. Also, Sadeghi-kiakhani et al. (2012) investigated chitosan-polypropylene imine (CS-PPI) as a biocompatible adsorbent biopolymer for the removal of textile dyes, namely, Reactive Black 5 (RB5) and Reactive Red 198 (RR198), and resulted in 97 and 99% of dye removal efficiency under optimal condition.

Zerovalent Zerovalent iron refers to the zero charges carried by each Fe atom. Nano zerovalent iron (nZVI) particle acts as a reducing agent which reduces Fe^{2+} and Fe^{3+}, and during the reduction process, the hydroxyl or hydrogen ions are generated which react with dye molecules and lead to breakage of chromophore (-N=N-) bond (Raman and Kanmani 2016). The degradation of textile dyes using nZVI particles depends on pH, nZVI dose, initial dye concentration, and dye volume (Samagata and Shah 2014). The efficiency of nZVI reactivity is improved, if the nZVI technique is integrated with other treatments like microwave radiation, ultrasonic irradiation, H_2O_2 oxidation, and UV illumination (Chen et al. 2011; Satapanajaru et al. 2011).

16.3.2.3 Nanocatalyst

Nanoparticles in the form of nanocatalyst have been enormously used in wastewater treatments as it possesses high catalytic efficiency, high surface area, mass transfer effect, effective enzyme storage, high surface reaction activity, and small size (1–100 nm) (Sharma et al. 2017). The various nanoparticles used for the treatment of textile effluent are tabulated in Table 16.5. A nanostructured catalyst medium which is sensitive to exposure of light is mainly employed to degrade textile pollutants present in wastewater. Such nanocatalyst works on the principle of photocatalysis. High photoactivity, nontoxicity, photostability, cost-effectiveness, and biologically and chemically inert are the properties of an ideal photocatalyst. Photocatalytic activity is produced by illuminating a semiconductor material to

Table 16.5 Various nanoparticles and their efficiency in treating textile effluent

Nanoparticles	Dye	Results	Reference
Silver nanoparticles	Textile industry effluent	Dye removal efficiency of silver nanoparticle using *S. nigrum* is 54.3% at pH 9.0 and 60 °C, whereas for silver nanoparticle using C. sativa is 25.3% at the same condition	Khatoon and Sardar (2017)
MgO	Azo	Removal was more than 98% under optimum operational conditions with dosage of 0.2 g, pH 8, and a contact time of 5 min for initial dye concentrations of 50–300 mg/L	Moussavi and Mahmoudi (2009)
Chitosan nanoparticles	Anthraquinone	The order of attractive forces was TPP > H_3O^+ > SO_3^- (in dye) > H bonds in acidic conditions and OH^- > TPP > SO_3^- (in dye) > H_2O in alkaline conditions	Hu et al. (2006)
Mesoporous aluminosilica monoliths	Organic or inorganic pollutants	The batch adsorption ofthe organic pollutants onto (10 g/L) adsorbents exhibits efficient removal of organic pollutants (e.g., aniline, p-chloroaniline, o-aminophenol, and p-nitroaniline) of up to 90%	El-safty et al. (2012)
Manganese dioxide	Methylene blue	The maximum adsorption capacity was 627.1 mg/g. the removal efficiency of MB increased along with increasing MnO_2 dose, whereas it decreased over pH 3.0–6.0	Qin et al. (2017)
MCM-22	Methylene blue, crystal violet, and rhodamine B	The adsorption capacities for MB, CV, and RB can reach 1.8×10^{-4}, 1.2×10^{-4}, and 1.1×10^{-4} Mol/g, respectively	Wang et al. (2006)
Polypropylene imine dendrimer	Direct red 80, acid green 25, acid blue 7, and direct red 23	Maximum dye releasing of 76.5% for DR80, 84.5% for AG25, 87% for AB7, and 93% for DR23 were achieved in aqueous solution at pH 12	Hayati et al. (2011)

(continued)

Table 16.5 (continued)

Nanoparticles	Dye	Results	Reference
Magnetic nanoparticles (MNP) with dendrimers	Reactive black 5	The maximum adsorption capacity of 70.423 mg g^{-1} in the aqueous solution of RBk5 at 25 °C	Zhou et al. (2013)
Chitosan-polypropylene imine dendrimer	Reactive black 5 and reactive red 198	The dye removal performance of 97 and 99% for RB 5 and RR 198, respectively	Sadeghi-kiakhani et al. (2012)
Bentonite-nZVI	Methyl orange	The removal rate of MO from wastewater was 99.75% when utilizing B-nZVI	Chen et al. (2011)
nZVI	Eriochrome blue black R (EBBR) – Azo dye	Complete decolorization of synthetic solutions contains 100 ppm EBBR by 0.3 g/L nZVI at initial pH solution 3 and occurred at 20 min ultrasonic irradiation	Taylor et al. (2014a)
nZVI-H_2O_2	Azo dye orange II	At optimal ph 3 and nZVI dose, 20 mg/L decolorization efficiencies were observed 98% TOC removal efficiencies of nZVI/H_2O_2 processes were 39% and 53% for a reaction time of 60 min	Moon et al. (2011)
Nano zerovalent iron	Reactive black 5 and reactive red 198	The removal efficiencies of both RB5 and RR198 were higher than 70% within 90 min. In a column experiment, decolorization efficiencies remained more than 80% up to 3.8 L and 3L of effluent volumes for RB5 and RR198, respectively	Satapanajaru et al. (2011)
Acrylic grafted polysulfone nanomembrane	Acid Orange 7, acid red 88, acid red 301, acid red 14, acid green 20, acid blue 113, acid red 18, acid blue 92, and acid Brown 214	The dye rejection and hydraulic permeability were 86–99.9% and 7.6 L m − 2 h − 1 bar−1, respectively	Amini et al. (2011)
Sodium p-styrene sulfonate	Acid Orange 10, acid red 4, direct red 80, disperse blue 56, and reactive Orange 16	Dye retention was higher than 97% and hydraulic permeability 0.23–0.28 m^3 m^{-2} d^{-1} at 0.4 MPa	Akbari et al. (2002)

(continued)

Table 16.5 (continued)

Nanoparticles	Dye	Results	Reference
Polysulfone membrane – Sodium p-styrene sulfonate (NaSS)	Acid Orange 10, acid red 4, basic blue 3, direct red 80, disperse blue 56, and reactive Orange 16	Dye retention was higher than 96%, and hydraulic permeability was 0.48–0.56m^{3}m^{-2} day^{-1} at 0.4 MPa	Akbari et al. (2006)
Polysulfone membrane – [2-(acryloyloxy) ethyl]-trimethyl ammonium chloride (AC)			
Polyamide nanomembrane	RB 15, RR 194, RY 145, RB 5, and RO 16	Filtration parameter like inlet flux range 7.8 and 9.2 ml/cm^2 s for 60 min at pH range 6.4–7.1 for dye concentration of 16 mg/l, 90–97% rejection rate of synthetic dye was observed	Taylor et al. (2014b)

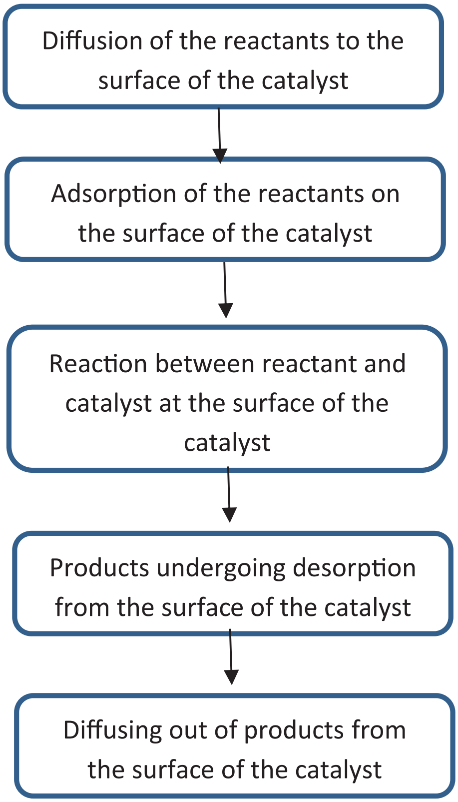


Fig. 16.4 General mechanism of photocatalysis

photons with energies equal to or larger than the semiconductors bandgap. This generates electron-hole pairs, which produces free radicals (e.g., OH^-) to undergo further reactions (Zheng et al. 2011). Photocatalysis is a surface phenomenon, and its general mechanism is explained in Fig. 16.4.

Nanostructured semiconductor photocatalyst usually used includes zinc oxide (ZnO), titanium dioxide (TiO_2), zinc sulfide (ZnS), ferric oxide (Fe_2O_3), and cadmium sulfide (CdS). Key areas in which photocatalysis can be applied for the treatment of textile effluent include the elimination of:

- Organic contaminants.
- Inorganic contaminants.
- Heavy metals.

Removal of Organic Contaminants Photocatalysis is used for the decomposition of harmful organic contaminants present in wastewater into harmless substances. The organic contaminants, like carboxylic acids, alcohols, phenolic derivatives, and chlorinated aromatic compounds, can be removed from textile wastewater using photocatalysis (Kumar et al. 2017). In this regard, semiconductor metal oxides structured as nanophotocatalyst such as TiO_2 and ZnO are proved to be successful. Silver nanocomposites have been successfully prepared by green route using two medicinal plant leaf extract, i.e., *Solanum nigrum* and *Cannabis sativa*. These biosynthesized silver nanocomposites were used for the removal of textile dyes (Khatoon and Sardar 2017).

Removal of Inorganic Contaminants It includes chemicals such as halide ions, cyanide, thiocyanate, ammonia, nitrates, and nitrites that can be effectively decomposed by photocatalytic reaction (Mills et al. 1982). The photocatalytic removal of toxic $CH_3Hg(II)Cl$ Hg(II)Cl and has been investigated using TiO_2 nanoparticles (Serpone et al. 1987).

Removal of Heavy Metals Major heavy metals present in wastewater from textile industries include copper, arsenic, lead, cadmium, mercury, and chromium. It has been reported that nickel oxide nanocatalyst is considered as a useful catalyst for the treatment of wastewater containing lead (Mahmoud et al. 2015). TiO_2 catalyst has been studied to recover gold (III), platinum (IV), and rhodium (III) chloride salts from wastewater effluent. A combination of activated carbon obtained from sewage sludge along with TiO_2 nanoparticles has been used to reduce Hg^{2+} ions followed by recovery of metallic Hg (P. Senthil Kumar et al. 2017).

16.3.2.4 Nanomembrane

Membranes play an important role in treatment of textile dyes present in waste water system includes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The selection of membrane for the treatment depends upon the pore size of the membrane. The main advantage of membrane-based technology is no requirement for the addition of chemicals. Suspended particles, debris, colloids, and many biological molecules, like sulfur, vat, and azoic dyes, are removed by means of MF and UF membrane at significantly low pressure. Organic and inorganic impurities from textile effluent are removed by RO, as it rejects more than 95% of ionic species (Amini et al. 2011; Thamaraiselvan and Noel 2014). Various nanofiltration membranes, at neutral pH, have negatively charged surface. NF membranes, pore size up to 2 nm, enable separation of salt solutions containing monovalent cations, divalent salts, low molecular weight organic compounds (200–1000 Da), and anions from the dye wastewater (Bruggen et al. 1999; All et al. 2006). The charges present on the surface of the membrane play an important role in permeation and rejection during membrane separation. This enables recovery and reuses tons of salts like NaCl used in dyeing industries. Molecular charge and polarity also have an effect on dye rejection (Bruggen et al. 1999). It has been studied that, in whatever proportion the reactive dye and NaCl used, the hydrolyzed reactive dyes and dye by-products were retained approximately 98% and the mineral salt recovery reached a rate of 98% (All et al. 2006). It has been reported that modified PSf membranes, using sodium p-styrene sulfonate monomer, were applied to treat colored textile effluents exhibiting acceptable performance in terms of flux and rejection. Dye rejection was higher than 96%, and hydraulic permeability was 0.48–0.56 m^3 m^{-2} day^{-1} at 0.4 MPa (Akbari et al. 2002, 2006). Amini et al. 2011 demonstrate the dye removal ability from colored textile wastewater by using polysulfone ultrafiltration membrane modified with acrylic acid and resulted 86–99.9% dye rejection and 7.6 L m^{-2} h^{-1} hydraulic permeability. Polyamide nanomembranes are applied and evaluated for removal of five different fiber reactive dyes found in wastewater, namely, reactive yellow 145, reactive blue 15, reactive black 5, reactive orange 16, and reactive red 194. The flux for all the samples ranged between 7.8 and 9.2 ml/cm^2 s (Taylor et al. 2014b). It was observed that the maximum dye rejection was up to 95–99% by using nanofiltration membrane NF45 and DK1073 (Lopes et al. 2005). Nanomembranes can be fabricated with nanoparticles to enhance the remediation efficiency in the aspect of permeability, catalytic reactivity, and fouling resistance. In recent times, high-temperature membrane distillation is also being investigated for dye wastewater treatment as part of zero liquid discharge (ZLD) strategy (Thamaraiselvan and Noel 2014). Though the nanofiltration is advantageous, membrane fouling is a drawback of filtration technique. Dyes introduce the undesirable flux decline by forming a colloidal fouling layer. With the help of feed pre-treatment modification and membrane cleaning, the process of membrane fouling can be prevented (P. Senthil Kumar et al. 2017).

16.4 Conclusions

The demand for better quality processed textile fabric has increased due to the modernization in the recent times across the globe. Therefore, there was an increasing load of waste generated from the textile-based industries. The textile industries waste and effluents are complex mixture in nature due to the presence of synthetic dyes, pigments, heavy metal compounds, and other uncharacterized metal salt complexes formed in the intermediate manufacturing processes. The increasing difficulty and complexity in treating textile wastes have led to a constant search for new techniques that are effective, eco-friendly, and economically viable. However, with the combination of nanotechnology, it become possible to remove both toxic properties and color of the dyes released into the environment.

References

Abou MF, El-trass A, El-sigeny S (2015) Synthesis of polyamidoamine dendrimer (PAMAM/CuS/AA) nanocomposite and its application in the removal of Isma acid fast yellow G Dye. 29. https://doi.org/10.1002/pat.3517

Afkhami A, Saber-tehrani M, Bagheri H (2010) Simultaneous removal of heavy-metal ions in wastewater samples using. J Hazard Mater 181(1–3):836–844. https://doi.org/10.1016/j.jhazmat.2010.05.089

Akbari A, Desclaux S, Remigy JC, Aptel P (2002) Treatment of textile dye effluents using a new photografted nanofiltration membrane. Desalination 149:101–107

Akbari A, Desclaux S, Rouch JC, Aptel P, Remigy JC (2006) New UV-photografted nanofiltration membranes for the treatment of colored textile dye effluents. 286:342–350. https://doi.org/10.1016/j.memsci.2006.10.024

Al-Fawwaz AT, Abdullah M (2016) Decolorization of methylene blue and malachite green by immobilized Desmodesmus sp. isolated from North Jordan. Int J Environ Sci Dev 7:95

Ali SAM, Akthar N (2014) A study on bacterial decolorization of crystal violet dye by *Clostridium perfringens*, *Pseudomonas aeruginosa* and *Proteus vulgaris*. Res Article Biol Sci 4:89–96

All C, Moulin P, Maisseu M, Charbit F (2006) Treatment and reuse of reactive dyeing effluents. 269:15–34. https://doi.org/10.1016/j.memsci.2005.06.014

Alvarez MS, Rodriguez A, Sanroman MA, Deive FJ (2015) Microbial adaptation to ionic liquids. RSC Adv 5(23):17379–17382

Amini M, Arami M, Mohammad N, Akbari A (2011) Dye removal from colored textile wastewater using acrylic grafted nanomembrane. Desalination 267(1):107–113. https://doi.org/10.1016/j.desal.2010.09.014

Anjum M, Miandad R, Waqas M, Gehany F, Barakat MA (2016) Remediation of wastewater using various nano- materials. Arab J Chem. https://doi.org/10.1016/j.arabjc.2016.10.004

Aragaw TA, Asmare AM (2018) Phycoremediation of textile wastewater using indigenous microalgae. Water Pract Technol 13(2):274–284

Babu BR, Parande AK, Raghu S, Kumar TP (2007) Cotton textile processing: waste generation and effluent treatment. Text Technol 11:141–153

Barr DP, Aust SD (1994) Mechanisms the white rot fungi use to degrade pollutants. Environ Sci Technol 28:79A–87A

Caparkaya D, Cavas L (2008) Biosorption of methylene blue by a brown alga Cystoseirabarbatula Kützing. Acta Chim Slov 55(3):547–553

Celia MP, Suruthi S (2016) Textile dye degradation using bacterial strains isolated from textile mill effluent. Int J Appl Res 2:337–341

Cengiz S, Cavas L (2008) Removal of methylene blue by invasive marine seaweed: *Caulerpa racemosa* var. cylindracea. Bioresour Technol 99(7):2357–2363

Chairin T, Nitheranont T, Watanabe A, Asada Y, Khanongnuch C, Lumyong S (2013) Biodegradation of bisphenol A and decolorization of synthetic dyes by laccase from white-rot fungus, Trametes polyzona. Appl Biochem Biotechnol 169(2):539–545

Chatha SA, Asgher M, Iqbal HM (2017) Enzyme-based solutions for textile processing and dye contaminant biodegradation—a review. Environ Sci Pollut Res 24(16):14005–14018

Chen H (2006) Recent advances in azo dye degrading enzyme research. Curr Protein Pept Sci 7(2):101–111

Chen Z, Jin X, Chen Z, Megharaj M, Naidu R (2011) Removal of methyl orange from aqueous solution using bentonite-supported nanoscale zero-valent iron. J Colloid Interface Sci 363(2):601–607. https://doi.org/10.1016/j.jcis.2011.07.057

Choo HK, Choi JS, Hwang DE (2007) Effect of coagulant types on textile wastewater reclamation in a combined coagulation/ultrafiltration system. Desalination 202(1–3):262–270

Chunfeng W, Jiansheng LI, Lianjun W, Xiuyun SUN (2009) Adsorption of dye from wastewater by zeolites synthesized from fly ash: kinetic and equilibrium studies. Chin J Chem Eng 17(3):513–521. https://doi.org/10.1016/S1004-9541(08)60239-6

Correia VM, Stephenson T, Judd JS (1994) Characterisation of textile wastewaters – a review. Environ Technol 15(10):917–929

Daneshvar N, Ayazloo M, Khataee AR, Pourhassan M (2007) Biological decolorization of dye solution containing Malachite Green by microalgae Cosmarium sp. Bioresour Technol 98(6):1176–1182

Deniz F, Karaman S (2011) Removal of an azo-metal complex textile dye from colored aqueous solutions using an agro-residue. Microchem J 99(2):296–302

Devi S, Murugappan A, Kannan RR (2016) Textile dye wastewater treatment using freshwater algae in packed-bed reactor: modeling. Desalin Water Treat 57(38):17995–18002. https://doi.org/10.1080/19443994.2015.1085910

Diller BG, Mogahzy YE, Inglesby MK, Zeronian SH (2016) Effects of scouring with enzymes, organic solvents, and caustic soda on the properties of hydrogen peroxide bleached cotton yarn. Text Res J 68(12):920–929

Duchemin B, Thuault A, Vicente A, Rigaud B, Fernandez C, Eve S (2012) Ultrastructure of cellulose crystallites in flax textile fibres. Cellulose 19(6):1837–1854

El-kassas HY (2014) Bioremediation of the textile waste effluent by Chlorella vulgaris. Egypt J Aquat Res 40:301–308

El-safty SA, Shahat A, Ismael M (2012) Mesoporous aluminosilica monoliths for the adsorptive removal of small organic pollutants. J Hazard Mater 201–202:23–32. https://doi.org/10.1016/j.jhazmat.2011.10.088

Elisangela F, Andrea Z, Fabio DG, de Menezes Cristiano R, Regina DL, Artur C-P (2009) Biodegradation of textile azo dyes by a facultative *Staphylococcus arlettae* strain VN-11 using a sequential microaerophilic/aerobic process. Int Biodeterior Biodegrad 63(3):280–288

Everts CJ, Kanwar RS (1994) Evaluation of rhodamine WT as an adsorbed tracer in an agricultural soil. J Hydrol 153:53–70. https://doi.org/10.1016/0022-1694(94)90186-4

Ezhilarasu A (2016) Textile industry dye degrading by bacterial strain Bacillus sp. Int J Adv Res Biol Sci 3(3):211–226

Falavarjani ER, Khorasani AC, Ghoreishi SM (2012) Microbial reduction of monoazo and diazo-linked dyes by *Pseudomonas aeruginosa* and *Pseudomonas putida*. J Pure Appl Microbiol 6:1559–1570

Ferreira BC, Teodoro FS, Mageste AB, Gil LF, de Freitas RP, Gurgel LV (2015) Application of a new carboxylate-functionalized sugarcane bagasse for adsorptive removal of crystal violet from aqueous solution: kinetic, equilibrium and thermodynamic studies. Ind Crop Prod 65:521–534

Ghaly AE, Ananthashankar R, Alhattab MVVR, Ramakrishnan VV (2014) Production, characterization and treatment of textile effluents: a critical review. J Chem Eng Process Technol 5:1–18

Ghosh S (2008) Extraction of azo dye molecules from aqueous solution using polyamidoamine dendrimer based polymeric network. J Chem Res 2008:419–421

Ghosh P, Samanta AK, Basu G (2004) Effect of selective chemical treatments of jute fibre on textile-related properties and processibility. Ind J Fibre Text Res 29(1):85–99

Gulati D, Jha I (2014) Microbial decolorization of dye reactive blue 19 by bacteria isolated from dye effluent contaminated soil. Int J Curr Microbiol App Sci 3:913–922

Gupta VK, Bhushan R, Nayak A, Singh P, Bhushan B (2014) Biosorption and reuse potential of a blue green alga for the removal of hazardous reactive dyes from aqueous solutions. Biorem J 18(3):179–191

Gupta VK, Tyagi I, Sadegh H, Shahryari-ghoshekandi R (2015) Nanoparticles as adsorbent; a positive approach for removal of noxious metal ions: a review. 34(3):195–214. https://doi.org/10.3923/std.2015.195.214

Harane RS, Adivarekar RV (2017) Sustainable processes for pre-treatment of cotton fabric. Text Cloth Sustain 2:2. https://doi.org/10.1186/s40689-016-0012-7

Hayati B, Mahmoodi NM, Arami M, Mazaheri F (2011) Dye removal from colored textile wastewater by poly(propylene imine) dendrimer: operational parameters and isotherm studies. 39(7):673–679. https://doi.org/10.1002/clen.201000182

Hemapriya J, Vijayanand S (2014) Ecofriendly bioremediation of a triphenylmethane dye by textile effluent adapted bacterial strain vp-64. Int J Curr Microbiol App Sci 3(9):983–992

Holkar CR, Jadhav AJ, Pinjari DV, Mahamuni NM, Pandit AB (2016) A critical review on textile wastewater treatments : possible approaches. J Environ Manag 182:351–366. https://doi.org/10.1016/j.jenvman.2016.07.090

Homyak GJL, Dutta J, Tabbals HF, Rao A (2008) Introduction to nanoscience. CRG Press, Boca Raton, FL

Hruby CE, Soupir ML, Moorman TB, Shelley M, Kanwar RS (2016) Effects of tillage and poultry manure application rates on *Salmonella* and fecal indicator bacteria concentrations in tiles draining Des Moines Lobe soils. J Environ Manag 171:60–69

Hu ZG, Zhang J, Chan WL, Szeto YS (2006) The sorption of acid dye onto chitosan nanoparticles. 47:5838–5842. https://doi.org/10.1016/j.polymer.2006.05.071

Hua M, Zhang S, Pan B, Zhang W, Lv L, Zhang Q (2012) Heavy metal removal from water/wastewater by nanosized metal oxides: a review. 212:317–331. https://doi.org/10.1016/j.jhazmat.2011.10.016

Imran M, Arshad M, Asghar HN, Asghar M, Crowley DE (2014) Potential of Shewanella sp. strain IFN4 to decolorize azo dyes under optimal conditions. Int J Agric Biol 16:578–584

Jilani S (2015) Bioremediation application for textile effluent treatment. 23(1):26–34. https://doi.org/10.5829/idosi.mejsr.2015.23.01.9227

Joshi N, Rathod M, Vyas D, Kumar R, Mody KH (2019) Multiple pollutants removal from industrial wastewaters using a novel bioflocculant produced by Bacillus licheniformis NJ3. Environ Prog Sustain Energy 38:S306–S314

Joutey NT, Bahafid W, Sayel H, Ghachtouli EN (2013) Biodegradation: involved microorganisms and genetically engineered microorganisms. In: Biodegradation-life of science. InTech, Rijeka

Kalaiarasi K, Lavanya A, Amsamani S, Bagyalakshmi G (2012) Decolourization of textile dye effluent by non-viable biomass of *Aspergillus fumigatus*. Braz Arch Biol Technol 55(3):471–476

Kandisa RV, Kv NS, Shaik KB, Gopinath R (2016) Bioremediation & biodegradation dye removal by adsorption: a review. 7(6). https://doi.org/10.4172/2155-6199.1000371

Karacakaya P, Kılıç NK, Duygu E, Dönmez G (2009) Stimulation of reactive dye removal by cyanobacteria in media containing triacontanol hormone. J Hazard Mater 172(2–3):1635–1639

Kerebo A, Desta A, Duraisamy R (2016) Removal of methyl violet from synthetic wastewater using nano aluminium oxyhydroxide. Int J Eng Res Dev 12(8):22–28

Khajeh M, Laurent S, Dastafkan K (2013) Nanoadsorbents: classification, preparation, and applications (with Emphasis on Aqueous Media). https://doi.org/10.1021/cr400086v

Khataee AR, Vafaei F, Jannatkhah M (2013) Biosorption of three textile dyes from contaminated water by filamentous green algal Spirogyra sp.: kinetic, isotherm and thermodynamic studies. Int Biodeterior Biodegrad 83:33–40. https://doi.org/10.1016/j.ibiod.2013.04.004

Khatoon N, Sardar M (2017) Efficient removal of toxic textile dyes using silver nanocomposites. J Nanosci: Curr Res 2(3):2–6

Kiliç NK, Dönmez G (2012) Remazol blue removal and EPS production by Pseudomonas aeruginosa and Ochrobactrum sp. Pol J Environ Stud 21(1)

Kochher S, Kumar J (2011) Microbial decolourization of crystal violet by Bacillus subtilis. Biol Forum Int J 3:82–86

Kumar KV, Sivanesan S, Ramamurthi V (2005) Adsorption of malachite green onto Pithophora sp., a fresh water algae: equilibrium and kinetic modelling. Process Biochem 40(8):2865–2872

Kumar PS, Narayan AS, Dutta A (2017) Nanochemicals and effluent treatment in textile industries. https://doi.org/10.1007/978-981-10-2188-6

Lade H, Govindwar S, Paul D (2015a) Low-cost biodegradation and detoxification of textile azo dye CI reactive blue 172 by *Providencia rettgeri* strain HSL1. J Chem

Lade H, Kadam A, Paul D, Govindwar S (2015b) Biodegradation and detoxification of textile azo dyes by bacterial consortium under sequential microaerophilic/aerobic processes. EXCLI J 14:158–174

Lavanya C (2014) Degradation of toxic dyes: a review. Int J Curr Microbiol App Sci 3(6):189–199

Liu L, Bilal M, Duan X, Iqbal HM (2019) Mitigation of environmental pollution by genetically engineered bacteria—current challenges and future perspectives. Sci Total Environ. 444–454 doi.org/https://doi.org/10.1016/j.scitotenv.2019.02.390

Lopes CN, Petrus JCC, Riella HG (2005) Color and COD retention by nanofiltration membranes. 172:77–83. https://doi.org/10.1016/j.desal.2004.07.030

Machado FM, De Pelotas UF, Bergmann CP, Adebayo M, State O (2012) Adsorption of a textile dye from aqueous solutions by carbon nanotubes adsorption of a textile dye from aqueous solutions by carbon nanotubes, (December). https://doi.org/10.1590/S1516-14392013005000204

Madhav S, Ahamad A, Singh P, Mishra PK (2018) A review of textile industry: wet processing, environmental impacts, and effluent treatment methods:31–41. https://doi.org/10.1002/tqem.21538

Mahapatra A, Mishra BG, Hota G (2013) Electrospun Fe 2 O 3 – Al 2 O 3 nanocomposite fibers as efficient adsorbent for removal of heavy metal ions from aqueous solution. J Hazard Mater:258, 116–259, 123. https://doi.org/10.1016/j.jhazmat.2013.04.045

Mahmoud AM, Ibrahim FA, Shaban SA, Youssef NA (2015) Adsorption of heavy metal ion from aqueous solution by nickel oxide nano catalyst prepared by different methods. Egypt J Pet. https://doi.org/10.1016/j.ejpe.2015.02.003

Manekar P, Patkar G, Aswale P, Mahure M, Nandy T (2014) Detoxifying of high strength textile effluent through chemical and bio-oxidation processes. Bioresour Technol 157:44–51

Mani S, Bharagava RN (2018) Textile industry wastewater: environmental and health hazards and treatment approaches, (December)

Marungrueng K, Pavasant P (2007) High performance biosorbent (Caulerpa lentillifera) for basic dye removal. Bioresour Technol 98(8):1567–1572

Mills A, Davies RH, Worsley D (1982) Water purification by semiconductor photocatalysis

Modi S, Pathak B, Fulekar MH (2015) Microbial synthesized silver nanoparticles for decolorization and biodegradation of azo dye compound. J Environ Nanotechnol 4:37–46

Moon B, Park Y, Park K (2011) Fenton oxidation of Orange II by pre-reduction using nanoscale zero-valent iron. Desalination 268(1–3):249–252. https://doi.org/10.1016/j.desal.2010.10.036

Moussavi G, Mahmoudi M (2009) Removal of azo and anthraquinone reactive dyes from industrial wastewaters using MgO nanoparticles. 168:806–812. https://doi.org/10.1016/j.jhazmat.2009.02.097

Nguyen AK, Fu CC, Juang SK (2016) Biosorption and biodegradation of a sulfur dye in high-strength dyeing wastewater by Acidithiobacillus thiooxidans. J Environ Manag 182:265–271

Oak U, Ghattargi V, Pawar S, Bhole B (2016) Degradation of Drimarene Red, a reactive textile dye by an extremophilic Bacillus sp. isolated from fresh water. Int J Appl Pure Sci Agric 2:105–113

Ozer A, Akkaya G, Turabik M (2006) The removal of acid red 274 from wastewater: combined biosorption and biocoagulation with Spirogyra rhizopus. Dyes Pigments 71(2):83–89

Pokharia A, Ahluwalia SS (2016) Decolorization of Xenobiotic Azo Dye-Black WNN by immobilized *Paenibacillus alvei* MTCC 10625. Int J Environ Bioremed Biodegrad 4:35–46

Prasad A, Rao KVB (2011) Physicochemical analysis of textile effluent and decolorization of textile azo dye by Bacillus endophyticus strain VITABR13. IIOAB J 2(2):55–62

Przystas W, Zablocka-Godlewska E, Grabinska-Sota E (2015) Efficacy of fungal decolorization of a mixture of dyes belonging to different classes. Braz J Microbiol 46(2):415–424

Qin Q, Sun T, Yin W, Xu Y (2017) Rapid and efficient removal of methylene blue by freshly prepared manganese dioxide. *Cogent Eng* 7:1–10. https://doi.org/10.1080/23311916.2017.1345289

Rajabi M, Mahanpoor K, Moradi O (2017) Removal of dye molecules from aqueous solution by carbon nanotubes and carbon nanotube functional groups : critical review. RSC Adv:47083–47090. https://doi.org/10.1039/c7ra09377b.

Rajendran R, Prabhavathy P, Karthiksundaram S, Pattabi S, Dinesh Kumar S, Santhanam P (2015) Biodecolorization and bioremediation of denim industrial wastewater by adapted bacterial consortium immobilized on inert polyurethane foam (PUF) matrix: a first approach with biobarrier model. Pol J Microbiol 64(4):329–338

Ramalingam S, Ponnusamy KS (2015) Novel adsorbent from agricultural waste (cashew NUT shell) for methylene blue dye removal: optimization by response surface methodology. Water Resources Ind 11:64–70

Raman CD, Kanmani S (2016) Textile dye degradation using nano zero valent iron : a review. J Environ Manag 177:341–355. https://doi.org/10.1016/j.jenvman.2016.04.034

Regan I (1962) Enzymes and their application in textile processing, especially desizing. J Soc Dye Colour 78(11):533–542

Rippon JA, Evans DJ (2012) Improving the properties of natural fibres by chemical treatments. In: Handbook of natural fibres. Oxford, Woodhead Publishing, pp 63–140

Robinson T, Chandran B, Nigam P (2002) Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. Water Res 36:2824–2830

Rott U, Minke R (1999) Overview of wastewater treatment and recycling in the textile processing industry. Water Sci Technol 40(1):137–144

Sadaf S, Bhatti HN, Bibi I (2013) Efficient removal of disperse dye by mixed culture of *Ganoderma lucidum* and *Coriolus versicolor*. Pak J Agr Sci 50:261–266

Sadeghi-kiakhani M, Arami M, Gharanjig K (2012) Dye removal from colored-textile wastewater using chitosan-PPI dendrimer hybrid as a biopolymer : optimization , kinetic , and isotherm studies:1–13. https://doi.org/10.1002/app.37615

Samagata S, Shah P (2014) Application of nanoscale zero-valent iron for wastewater treatment. Int Conf Multidiscip Res Pract I(VII):342–344

Saratale RG, Saratale GD, Chang JS, Govindwar SP (2011) Bacterial decolorization and degradation of azo dyes: a review. J Taiwan Inst Chem Eng 42(1):138–157

Sarayu K, Sandhya S (2010) Aerobic biodegradation pathway for Remazol Orange by *Pseudomonas aeruginosa*. Appl Biochem Biotechnol 160(4):1241–1253

Satapanajaru T, Chompuchan C, Suntornchot P, Pengthamkeerati P (2011) Enhancing decolorization of reactive black 5 and reactive red 198 during nano zerovalent iron treatment. Desalination 266(1–3):218–230. https://doi.org/10.1016/j.desal.2010.08.030

Senthilkumar S, Perumalsamy M, Prabh HJ (2014) Decolourization potential of white-rot fungus *Phanerochaete chrysosporium* on synthetic dye bath effluent containing Amido black 10B. J Saudi Chem Soc 18:845–853

Serpone N, Ah-You YK, Tran TP, Harris R, Pelizzetti E, Hidaka R (1987) AM1 simulated sunlight photoreduction and elimination of Hg(II) and CH3Hg(II) chloride salts from aqueous suspensions of titanium dioxide. Sol Energy 39(6):491–498

Sethi S, Malviya MM, Sharma N, Gupta S (2012) Biodecolorizationof azo dye by microbial isolates from textile effluent and sludge. Univers J Environ Res Technol 2(6):582–590

Shah M (2014) Efficacy of Rhodococcus rhodochrous in microbial degradation of toludine dye. J Pet Environ Biotechnol 5(4):187

Sharma N, Bhatnagar P, Chatterjee S, John PJ, Soni IP (2017) Bio nanotechnological intervention : a sustainable alternative to treat dye bearing waste waters. Ind J Pharm Biomed Sci (IJPBR) 5(1):17–24

Sharma R, Sharma S (2015) Biosorption of Alizarin by Burkholderia sp. Int J Curr Microbiol App Sci 4:112–122

Shinkafi MS, Mohammed IU, Audu AA (2015) Degradation and decolourization of textile dyes effluents. Eur J Biotech Biosci 3:06–11

Singh L, Singh VP (2010) Microbial degradation and decolorization of dyes in semi-solid medium by the fungus–*Trichoderma harzianum*. Environ We Int J Sci Tech 5:147–153

Singh AK, Singh R, Soam A, Shahi SK (2012) Degradation of textile dye orange 3R by Aspergillus strain (MMF3) and their culture optimization. Curr Disc 1:7–12

Sinha S, Nigam S, Singh R (2015) Potential of Nostocmuscorum for the decolorisation of textiles dye RGB-red. Int J Pharm Bio Sci 6:1092–1100

Song ZY, Zhou JT, Wang J, Yan B, Du CH (2003) Decolorization of azo dyes by Rhodobactersphaeroides. Biotechnol Lett 25(21):1815–1818

Tahir H, Sultan M, Jahanzeb Q (2008) Removal of basic dye methylenblue byusing bioabsorbents Ulva lactuca and Sargassum. Afr J Biotechnol 7:2649–2655

Taleb M, El-Trass A, El-Sigeny S (2015) Synthesis of polyamidoamine dendrimer (PAMAM/CuS/AA) nanocomposite and its application in the removal of Isma acid fast yellow G Dye. Polym Adv Technol 2015(26):994–1002

Tanapongpipat A, Khamman C, Pruksathorm K, Hunsom M (2008) Process modification in the scouring process of textile industry. J Clean Prod 16(1):152–158

Taylor P, Khaloo SS, Fattahi S (2014a) Enhancing decolorization of Eriochrome Blue Black R during nano-size zero-valent iron treatment using ultrasonic irradiation. Desalin Water Treat:37–41. https://doi.org/10.1080/19443994.2013.801322

Taylor P, Rashidi HR, Sulaiman NMN, Hashim NA, Hassan CRC, Ramli MR (2014b) Synthetic reactive dye wastewater treatment by using nano-membrane filtration. Desalin Water Treat:37–41. https://doi.org/10.1080/19443994.2014.912964

Thamaraiselvan C, Noel M (2014) Membrane processes for dye wastewater treatment; recent progress in fouling control:37–41. https://doi.org/10.1080/10643389.2014.900242

Thanunchanok C, Thitinard N, Akira W, Yasuhiko A, Chartchai K, Saisamorn L (2014) Purification and characterization of the extracellular laccase produced by WR710-1 under solid-state fermentation. J Basic Microbiol 54(1):35–43

Tunc O, Tanacı H, Aksu Z (2009) Potential use of cotton plant wastes for the removal of Remazol Black B reactive dye. J Hazard Mater 163:187–198

Tzanov T, Calafell M, Gübitz G, Cavaco-Paulo A (2001) Bio-preparation of cotton fabrics. Enzym Microb Technol 29:357–362

Uday US, Bandyopadhyay TK, Bhunia B (2016) Bioremediation and detoxification technology for treatment of Dye (s) from textile effluent. In: Textile wastewater treatment. InTech, Rijeka

Van Der Bruggen B, Schaep J, Wilms D, Vandecasteele C (1999) Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. J Membr Sci 156:29

Vitor V, Corso CR (2008) Decolorization of textile dye by Candida albicans isolated from industrial effluents. J Ind Microbiol Biotechnol 35(11):1353–1357

Wang N, Chu Y, Wu F, Zhao Z, Xu X (2017) Decolorization and degradation of Congo red by a newly isolated white rot fungus, *Ceriporia lacerata,* from decayed mulberry branches. Int Biodeterior Biodegrad 117:236–244

Wang S, Li H, Xu L (2006) Application of zeolite MCM-22 for basic dye removal from wastewater. 295:71–78. https://doi.org/10.1016/j.jcis.2005.08.006

Waring RD, Hallas G (2013) The chemistry and application of dyes. Springer Science & Business Media, Berlin

Xu M, Guo J, Kong X (2007a) Fe (III)-enhanced Azo reduction by Shewanella decolorationis S12:1342–1349. https://doi.org/10.1007/s00253-006-0773-z

Xu M, Guo J, Sun G (2007b) Biodegradation of textile azo dye by Shewanella decolorationis S12 under microaerophilic conditions:719–726. https://doi.org/10.1007/s00253-007-1032-7

Yang YH, Jia BR, Chen B, Li L, (2014) Degradation of recalcitrant aliphatic and aromatic hydrocarbons by a dioxin-degrader *Rhodococcus* sp. strain p52. Environmental Science and Pollution Research 21 (18):11086–11093.

Zheng H, Ou JZ, Strano MS, Kaner RB, Mitchell A (2011) Nanostructured tungsten oxide – properties, synthesis, and applications. Adv Funct Mater 21(12):2175–2196

Zhou SL, Li J, Hong G, Chang C (2013) Dendrimer modified magnetic nanoparticles as adsorbents for removal of dyes:6814–6819. https://doi.org/10.1166/jnn.2013.7784

Removal of Dyes from Industrial Effluents by Application of Combined Biological and Physicochemical Treatment Approaches

17

Modhurima Misra, Kriti Akansha, Ashish Sachan,
and Shashwati Ghosh Sachan

Abstract

One of the major crises that the world is facing today is environmental pollution. Synthetic dyestuffs find uses in various industries like textile, cosmetics, leather, paper printing, tannery, food coloring, etc. Recalcitrant azo dyes (-N=N-) are the predominant class of molecules used because of their color fastness, persistence in aquatic environment, stability, and resistance to degradation. These detrimental compounds are quite complex and structurally diverse, containing azoic linkages. It is evident from prior researches that these dyes and their by-products, specifically the aromatic amines, which result due to the reductive cleavage of the azo bonds, are classified as extremely toxic, carcinogenic, mutagenic, and genotoxic to humans and aquatic biota and are also capable of causing serious skin irritations. They inhibit aquatic photosynthesis by obstructing light penetration, deplete dissolved oxygen (DO) level, and compromise both aesthetics and ecological balance of water bodies. Dye-laden wastewater from industries is often released into the environment, untreated or poorly treated, to avoid the complexity and investment of capital for setting up of treatment plants, thus absolutely defying the environmental standards. The developing and underdeveloped countries are exposed to a bigger risk as they are being exploited as lucrative spots for the development of production sites by the textile industries to lower the production costs. The existing processes for color removal consist of physical, chemical, and physicochemical ones, the recent addition to the list being the biological means. Though the accepted techniques are quite capable, yielding satisfactory

---

M. Misra · K. Akansha · S. G. Sachan (✉)
Department of Bio-Engineering, Birla Institute of Technology, Ranchi, Jharkhand, India
e-mail: ssachan@bitmesra.ac.in

A. Sachan
Centre for Life Sciences, Central University of Jharkhand, Ranchi, Jharkhand, India
e-mail: ashish.sachan@cuj.ac.in

M. Shah, A. Banerjee (eds.), *Combined Application of Physico-Chemical & Microbiological Processes for Industrial Effluent Treatment Plant*,
https://doi.org/10.1007/978-981-15-0497-6_17

results, each of them has their fair shares of advantages and disadvantages. Till now, a single, universal method, capable of complete degradation of these dyestuffs and being economically feasible at the same time, is far out of reach. While the various physicochemical methods are established industrially, they often generate huge amount of sludge as secondary pollutants, apart from being cost and energy intensive. Thus, focus has been shifted toward the exploitation of the capability of the vast array of biological entities for remediation of these toxic compounds. Biological means, though cheap and are able to completely mineralize the dyes, are often restricted to the lab scale. In search of effective treatment procedures, researchers are targeting the already existing methods and combining them for the development of potential hybrid technologies.

Keywords
Industrial effluents · Removal of dyes · Conventional treatments · Hybrid wastewater treatment strategies

17.1 Introduction

Even though we belong to the world of technological advancement, environmental pollution, be it air, water, or soil, is one of the prominent problems that the world is facing today. With the advent of urbanization, industrialization, and unprecedented population growth, the pollution of water bodies has reached to new heights, wherein the availability of water, more so fresh water, has become a serious crisis all over the world. The addition of contaminated water from various industries into the water bodies has fueled the gradual deterioration of the water quality in many countries. In the developing countries, it is a big issue as the industrial effluents are released into the environment, untreated or without proper treatment, to avoid the complexity and investment of capital for setting up of treatment plants, thus absolutely defying the environmental standards. Water pollutants include domestic wastes, dyes, toxic organics, insecticides, pesticides, chemical wastes, heavy metals, volatile organic carbon (VOC), etc. Among these, synthetic dyes are significant contributors as their annual production rate is quite high, around 7×10^5 tons, and they are employed in various industries like textile, cosmetics, leather, paper printing, tannery, food coloring, etc. (Lourenço et al. 2001). Previously natural organic dyes derived from plants, mushrooms, lichens, etc. were in use, but toward the beginning of the twentieth century, synthetic dyestuffs started replacing them due to cost-effectiveness in their synthesis and that numerous colorants can be obtained. Nowadays there are more than 100,000 commercially available dyes. The textile industry accounts for two-third of the total dyestuff market (Lourenço et al. 2001) and significantly generates contaminated effluents (Robinson et al. 2001). Textile wastewater is very diverse in chemical composition due to the presence of large number of dyes and numerous chemical reagents used in processing (Joshi et al. 2004). The sanitation of textile effluents is necessary not only to remove the toxic chemicals present but also to recycle and reuse the water as this industry consumes large volumes of water. Azo dyes are the frequently used group of colorants and represent over 60% of the total dyes used (Fu and Viraraghavan 2001) as they are highly stable in presence of water, air, and sunlight. Recent studies have confirmed that over 4.5×10^6 tons of azo dyes and their by-products are released into the environment annually in the form of textile effluent which is of significant concern (Rawat et al. 2016). These detrimental aromatic compounds are recalcitrant in nature, complex, and structurally diverse, containing azoic linkages (-N=N-). These dyes and their metabolic intermediates like aromatic amines, which result due to the reductive cleavage of the azo bonds, are known to be toxic, carcinogenic, mutagenic, and genotoxic to humans (Daneshvar et al. 2003). Many of these are even manufactured from known carcinogens like benzidine and other aromatic compounds (Robinson et al. 2001). Dyes and their degradation products are capable of causing several human health disorders such as nausea, hemorrhage, ulceration of skin and mucous membranes (Solpan et al. 2003), and severe damage to the kidney, liver, brain, reproductive system, and central nervous system (Kadirvelu et al. 2003). Studies have shown that even in very trace concentration (1 mg/L) (Pandey et al. 2007), dyes are visible in aquatic systems due to high tinctorial value and compromise the aesthetic merits of the water resources (Joshi et al. 2004). The colored wastewater is a prominent source of eutrophication and disturbances in aquatic life (Gemeay et al. 2003). They interfere with the penetration of sunlight and gas solubility, inhibit aquatic photosynthesis, and deplete the level of dissolved oxygen, thus considered harmful for the growth of aquatic flora and fauna. Concerns stemming from the hazardous effects of dyes have led to more stringent regulations for discharge of colored wastewater. In line with the pollution minimization efforts, endless researches are going on for the development of effective wastewater treatment methods. The existing processes for color removal consist of physical, chemical, and physicochemical ones, the recent addition to the list being the biological means, but none of them has emerged fully successful (Hao et al. 2000). Moreover, they often generate huge amount of sludge as secondary pollutants, apart from being cost and energy intensive. Biological options, though cost-competitive and environment-friendly, are rather inefficient in decolorizing the dyes (Hai et al. 2007). Till now, a single, universal method, capable of complete degradation of these dyestuffs and being economically feasible at the same time, is far out of reach because of the enhanced properties of the dyes which make them resistant to chemical, photocatalytic, and biological degradation (Savin and Butnaru 2008). In search of effective treatment procedures, recent researches are targeting the already existing methods and combining them for the development of potential hybrid technologies. Different physicochemical methods alone or along with various other advanced oxidation processes (AOPs) are being coupled and implemented for treating dye wastewater. Even biological systems, with combinations among themselves or fused with the existing physicochemical and AOPs, are also being employed for attractive outcomes (Hai et al. 2007). Extensive research is required in this area before a substantial solution can be formulated. This review deals with the most important existing technologies for color removal, their combined and hybrid forms, and their merits and demerits in brief.

17.2 Classification of Synthetic Dyes

Dyes may be classified according to their chemical structure or by their usage or application. The former approach is adopted by dye chemists, while the latter one is usually taken up by the dye technologist (Hunger 2003).

17.2.1 Chemical Classification

It is the most appropriate system for the classification of dyes and is advantageous as it readily identifies dyes belonging to a group that has characteristic properties, for example, azo dyes (strong, cost-effective), anthraquinone dyes (weak, expensive), etc. The different groups of dyes are azo, anthraquinone, triphenylmethane, vat, xanthenes, indigoid, sulfur, polymethine, nitroso, aryl carbonium, diphenylmethane, phthalocyanine, heterocyclic, nitro, etc.

17.2.2 Usage Classification

Classification by usage or application to fabrics is the principal system adopted by the Colour Index (Saini 2017). Table 17.1 summarizes the classification of dyes according to their usage which is arranged according to the C.I. application classification. It shows the main substrates, the methods of application, and the representative chemical types of each class.

17.3 Physical Basis of Color

Dyes absorb color in the range of 400–700 nm, i.e., in the visible range of the spectrum. These molecules have a conjugated structure with alternate single and double bonds, and resonance of electrons stabilizes the compounds. It possess chromophores, the prominent group which is responsible for imparting color (Aksu and Tezer 2005) and auxochromesS that will influence the solubility of the dyes and act as color enhancer (Bhatia et al. 2017). Chromophore undergoes π–$\pi*$ and n–$\pi*$ transitions, whereas auxochromes can only undergo transition of n electrons. The functional groups of chromophores are –N=N–, –C=O, –NO2, and $O{=}(C_6H_4){=}O$ (quinoid assemblies), while those present in auxochromes are –NH3, –COOH, –OH, and –SO3H (Marmagne and Coste 1996).

17.4 Dye Removal Technologies

Removal of color from dye effluent has become a pertinent problem and was quite a challenge since the past few decades. The remediation of dye wastewater deals with not only the removal of color but also the degradation and mineralization of those

Table 17.1 Usage classification of dyes

Class	Principal substrates	Method of application	Chemical types
Acid	Nylon, wool, silk, paper, inks, and leather	Usually from neutral to acidic dyebaths	Azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro, and nitroso
Azoic components and compositions	Cotton, rayon, cellulose acetate, and polyester	Fiber impregnated with coupling component and treated with a solution of stabilized diazonium salt	Azo
Basic	Paper, polyester, polyacrylonitrile, modified nylon, and inks	Applied from acidic dyebaths	Cyanine, azo, azine, hemicyanine, anthraquinone, diphenylmethane, diazahemicyanine, acridine, triarylmethane, xanthene, and oxazine
Direct	Cotton, rayon, paper, leather, and nylon	Applied from neutral or slightly alkaline baths containing additional electrolyte	Azo, phthalocyanine, stilbene, and oxazine
Disperse	Polyester, plastics, polyamide, acetate, and acrylic	Fine aqueous dispersions often applied by high temperature/pressure or lower temperature carrier methods; dye may be padded on cloth and baked on or thermofixed	Azo, anthraquinone, styryl, nitro, and benzodifuranone
Fluorescent brighteners	Soaps and detergents, oils, all fibers, paints, and plastics	From solution, dispersion, or suspension in a mass	Stilbene, pyrazoles, coumarin, and naphthalimides
Food, drug, and cosmetic	Foods, drugs, and cosmetics		Azo, anthraquinone, carotenoid, and triarylmethane
Mordant	Wool, leather, and anodized aluminum	Applied in conjunction with Cr salts	Azo and anthraquinone
Oxidation bases	Hair, fur, and cotton	Aromatic amines and phenols oxidized on the substrate	Aniline black and indeterminate structures
Reactive	Cotton, wool, silk, and nylon	Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline)	Azo, anthraquinone, phthalocyanine, formazan, oxazine, and basic

(continued)

Table 17.1 (continued)

Class	Principal substrates	Method of application	Chemical types
Solvent	Plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils, and waxes	Dissolution in the substrate	Azo, triphenylmethane, anthraquinone, and phthalocyanine
Sulfur	Cotton and rayon	Aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur-containing products on fiber	Indeterminate structures
Vat	Cotton, rayon, and wool	Water-insoluble dyes solubilized by reducing with sodium hydrogensulfite, then exhausted on fiber, and reoxidized	Anthraquinone (including polycyclic quinones) and indigoids

Adopted from Industrial Dyes Chemistry, Properties, Applications edited by Klaus Hunger, p 4

toxic compounds so that their impact on the environment can be lessened (Asgher et al. 2008). Numerous technologies have been developed for the sanitation of colored effluents, each having their shares of advantages and disadvantages (Ayed et al. 2009). The economic feasibility of any technique, used for color removal, depends upon structure of the dye molecule, composition of the effluent, environmental fate, handling, etc. (Cassidy et al. 1996). The existing treatment methods can be broadly classified under three main categories as shown in Fig. 17.1. The physical treatment methods employ the application of physical forces for the separation of dye molecules from wastewater, while the chemical treatments are mediated through chemical reactions by addition of chemical reagents like chlorines, ozone, Fenton's

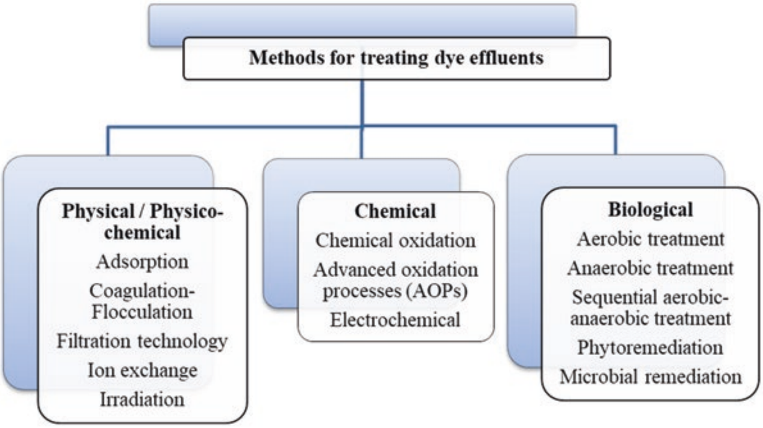


Fig. 17.1 Treatment strategies for removal of color from dye effluents

reagents, UV/peroxide, UV/ozone, etc. Biological treatments include degradation of pollutants by microbes or plants or enzymatic degradation under aerobic or anaerobic conditions.

17.4.1 Physical/Physicochemical Methods

17.4.1.1 Adsorption

This process is one of the most sought-after physical treatment techniques for colored effluent treatment because of its effectiveness, simplicity, and economic feasibility. The process involves the transfer and accumulation of soluble organic dyes from wastewater to the surface of the solid and highly porous adsorbent (Saini 2017). Adsorption is mainly of two types – physisorption and chemisorptions. Physical adsorption is a temporary, easily reversible phenomenon which results due to weak intermediate bonds between the adsorbate and adsorbent like van der Waals interactions, hydrogen bonding, and dipole–dipole interactions. Chemical adsorption is mostly irreversible in nature and occurs when there are strong forces of interaction between the adsorbate and the adsorbent due to electron exchange. Examples of such bonds are covalent and ionic bonds (Shah 2018). The adsorbent has a threshold capacity beyond which it cannot adsorb further and is generally regarded as “spent” and it should be replaced by new material. The spent adsorbent must be disposed either by regeneration or incineration (Saini 2017). The main factors which influence dye adsorption are interaction between dye and adsorbent, surface area and particle size of adsorbent, pH, temperature, and time duration of contact. The use of a particular adsorbent for the removal of substances from the liquid phase depends upon the equilibrium between adsorbed and free species (Joshi et al. 2004). Activated carbon is the most preferred sorbent in remediating effluents as it can remove different types of dyes and is inert to the toxic chemicals present in the effluent, but due to its high cost, researchers are looking forward to new low-cost alternatives, though they have less adsorptive capacity. In the recent years, studies on adsorptive removal of textile dyes have been carried out using various agricultural products, by-products, and wastes such as wheat straw (Robinson et al. 2002), cotton (Tunc et al. 2009), leaves of pine trees (Deniz and Karaman 2011), sugarcane bagasse (Ferreira et al. 2015), shells of cashew nut (Subramaniam and Ponnusamy 2015), industrial and agricultural wastes, wood bark, clay (Lisi et al. 2007), peach stones (Attia et al. 2008), rice husks (Rahman et al. 2005), groundnut shell-based activated carbon (Malik et al. 2007), prehydrolyzed beech sawdust (Batzias and Sidiras 2007), sawdust (Malik 2003), pine sawdust (Ozacar and Sengil 2005), sepiolite (Dŏgan et al. 2007), sand (Rauf et al. 2007), alkaline white mud (Zhu et al. 2007), ethylenediamine-modified rice hull (Ong et al. 2007), calcium metasilicate, activated sludge, activated alumina, bauxite, dolomite, silica (Forgacs et al. 2004), chitin (Akkaya et al. 2007), steel plant slag, bentonite clay (Ramakrishna and Viraraghavan 1997), sugarcane dust (Ho et al. 2005), etc. Moreover microbial biomass is being sought after as a potent biosorbent (Han and Yun 2007). The adsorptive capacity of a large number of organic and inorganic supports has been studied. Inorganic supports are mechanically and chemically stable with a high specific area and are resistant to microbial degradation, whereas the organic ones are renewable in nature (Forgacs et al. 2004). The extent to which a particular dye will be adsorbed by a specific support is governed by the molecular weight as well as the solubility of the dye. For instance, hydrophilic, polar dyes are usually poorly adsorbed by nonpolar carbon. The rate of adsorption of low molecular mass, acid, and reactive dyes is less as compared to that of high molecular weight basic and direct dyes. The rate of adsorption for hydrophobic disperse dyes is moderate to high (Singh and Arora 2011). A cyclic polymer of glycouril and formaldehyde, called cucurbituril, has shown excellent sorption capacity for numerous textile dyes (Joshi et al. 2004). It has an internal hydrophobic cavity and acts as a dye complexing agent. It can adsorb reactive dyes by forming host–guest complexes (Singh and Arora 2011). It can form complexes in the presence of other organic compounds in the effluent, but its high cost is the major shortcoming.

17.4.1.2 Coagulation–Flocculation

These techniques are frequently used for the separation of suspended solids from wastewater (Cho et al. 2003). Suspended solids having similar surface charge repel each other and tend to settle out in the effluent. This can be prevented by the use of proper coagulant. In this process, the charge on the suspended solids is neutralized by the addition of suitable coagulants bearing opposite charge which results in the formation of flocculated agglomerates (Meyers 1998). Flocculation is a gentle mixing stage in which unstable particles bind to form a floc that can be easily removed from the suspension by filtration or sedimentation (Crini 2006; Culp and Beland 1996). The size of the floc gradually increases with repeated collisions and interactions with inorganic or organic polymers. Salts of iron and aluminum are the most commonly used inorganic coagulants. Synthetic polyelectrolytes, fly ash, and clay are also used as a thickening agent (Daneshvar et al. 2003). The major disadvantages of this process are that inorganic coagulants are quite ineffective to remove highly soluble dyes (Daneshvar et al. 2003) from the textile wastewater, generation of colored coagulates having disposal issues, generation of secondary pollutants (Shah 2018), toxicity of the sludge, and increase in the TDS of treated effluent (Singh and Arora 2011). The aluminum and iron salt-enriched sludge produced from coagulation treatment are reported to be toxic to aquatic biota, specially the daphnids and larvae and eggs of fish (Dalzell and MacFarlane 1999; Randall et al. 1999; Van Anholt et al. 2002). Moreover color removal occurs partially, and reduction of COD depends on the type of coagulant used. Coagulation–flocculation methods were successfully applied for color removal of water-insoluble sulfur and disperse dyes, whereas for water-soluble dye classes, the results were not satisfactory (dos Santos et al. 2007). In this process the dye molecules undergo simple separation without any decomposition.

17.4.1.3 Membrane Processes/Filtration Technology

This is the principle technique used for generating safe drinking water and is used in wastewater treatments. It consists of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverses osmosis (RO). MF is not effective for wastewater treatment because the membrane used in this process has large pore size. For the separation and recycling of water-insoluble dyes like indigo and disperse dyes, UF has been employed, whereas hydrolyzed reactive dyes have been successfully removed from textile effluent using NF and RO processes (Singh and Arora 2011). Membranes allow the removal and reuse of dyes, auxiliary chemicals used in the dyeing process, and processed water. Studies reveal that this process has been used for the removal of water-soluble dyes (Joshi and Purwar 2004). The type of membrane system used for the separation process depends on several factors like dyeing process, nature of the dye, the chemical composition of the waste stream, and the maximum allowable expenditure (Diaper et al. 1996). The membranes used for the removal of dye molecules are manufactured in such a manner that they can tolerate various solvents and chemicals, are thermostable, and can withstand the change in pH over a wide range. Membranes for RO and UF are usually prepared from variety of polymers like polyamides, polyacrilonitrile, polysulphonates, polycarbonate, polypropylene, fluorocarbon-based polymers, etc. (Joshi and Purwar 2004). Polysulphonate ultrafiltration membranes were prepared by phase inversion method under different temperatures from 25 to 65 °C. When these are used in the treatment of real textile effluent, membrane produced under 65 °C was able to remove 99% color along with equal amount of COD (Koseoglu-Imer 2013). The main advantage of this technology is that no additional chemicals are used. This is a physical process of color removal, in which the colorants are separated and concentrated from the effluents without their degradation and require subsequent disposal. However, filtration technique is cost and energy intensive, and the short membrane life as well as membrane fouling leading to frequent regeneration is an impediment in the widespread usage of this technology. Fouling occurs when there is clogging of membrane pores which causes a subsequent reduction in flux and increase in head loss (Amini et al. 2011). Decline in flux can result from the accumulation of salts from textile effluents in the membrane (internal concentration polarization) and on the membrane surface (external concentration polarization) which can be prevented by the frequent washing of the membrane by suitable antiscaling solution. The types of membranes used for different filtration purposes, along with their application, are enlisted in Table 17.2.

Table 17.2 Types of membranes used in different filtration techniques and their applications (Kraume 2002)

Filtration technique	Membrane type	Applications
Microfiltration	Porous membrane	Separation of suspended solids
Ultrafiltration	Porous membrane	Concentration, fractioning, and treatment of macromolecules in fluid systems
Nanofiltration	Nonporous membrane	Fractioning of dissolved materials in fluid systems
Reverse osmosis	Solution–diffusion membrane	Concentration of dissolved materials in fluid systems

17.4.1.4 Ion Exchange

Dyes are mostly acidic or basic in nature, so theoretically suitable ion exchange resins can be used for their separation. These dyes should ideally form flocs with the ion exchangers that can be separated by filtration technique. A large number of agricultural residues like waste banana pith, water hyacinths, maize cob, coir pith, sugar beet fiber and eucalyptus bark (Crini 2006), sunflower stalks (Weixing et al. 1998), and soybean pulp (Kumar 2006) have been experimented upon such that they can be modified, and properties of ion exchangers can be induced in them, following which they can be used for the decolorization of textile effluents (Singh and Arora 2011). But ion exchangers are not much used in treating dye effluents as they cannot accommodate wide range of dyes due to presence of various additives in wastewater, produce large amount of sludge, and are ineffective for water-insoluble disperse dyes and the fact that they have to be regenerated using costly solvents when they are saturated makes them all the more unfavorable for wastewater treatments. Moreover, compared to activated carbon, these resins possess poor hydrodynamic properties.

17.4.1.5 Irradiation

In this technique these radiations from monochromatic UV lamps functioning under 253.7 nm are used for the elimination of different organic pollutants (Saini 2017). In decolorization of dyehouse wastewater, gamma radiation has been used. The dyes that are resistant to chemical oxidation or reduction processes can be degraded by this technique. The rate of degradation depends upon the radiation dose and the availability of oxygen supply (Meyers 1998; Perkowski and Kos 2003). A large amount of dissolved oxygen is necessary for the effective breakdown of an organic dye by irradiation, so this method needs a constant and adequate supply of oxygen. It has been successfully used for the removal of reactive, acid, and disperse dyes (Joshi and Purwar 2004). Catalyst titanium dioxide is reported to enhance the efficiency of the said process (Krapfenbauer et al. 1999). Photocatalytic degradation of dyes like CI Basic Blue 9, CI Acid Orange 10, and CI Reactive Blue 19 using solar radiations have been investigated and are found to be cost-effective with respect to the artificial UV radiation (Joshi and Purwar 2004).

17.4.2 Chemical Methods

17.4.2.1 Chemical Oxidation

Oxidation is the most widely studied chemical decolorization. It is a simple process in which the dye molecules are mineralized into carbon dioxide, water, nitrogen, aldehydes, acids, and sulfates depending on the dye structure and on the strength of the oxidant employed (Uygur 1997). The frequently used oxidizing agents are chlorine and chlorine dioxide, ozone, hydrogen peroxide, and permanganate (Xu et al. 2005).

- *Oxidation with Chlorine*

Water-soluble dyes (e.g., acid, direct, metal complex dyes) have been decolorized using chlorine in the form of sodium hypochlorite, but water-insoluble disperse and vat dyes are found to be resistant to chlorine decolorization (Namboodri et al. 1994a, b). Decolorization of reactive dyes, on the other hand, requires long treatment time (Hassan and Hawkyard 2007). Dyes having amino or substituted amino chromophores rapidly undergo chlorine decolorization. However, chlorine treatment gives rise to toxic chlorinated organics such as halogenated hydrocarbons that are hazardous to humans as well as the environment.

- *Oxidation with Ozone*

Ozone is a very powerful oxidizing agent, widely used because of its high reactivity and shows good color removal efficiencies (Alaton et al. 2002). Ozone quickly decolorizes water-soluble dyestuffs but with non-soluble dyestuffs reacts much slower. It attacks the unsaturated bonds of the chromophores leading to partial mineralization of the dyes. The by-products formed out of such reaction are organic acids, aldehydes, and ketones. Chemical sludge is not formed, and residual ozone can easily be converted to oxygen (Singh and Arora 2011).

- *Oxidation with Hydrogen Peroxide*

Another oxidizing agent that is frequently used in wastewater treatment is hydrogen peroxide (H_2O_2). Hydrogen peroxide treatment is suitable for the oxidative decolorization of most of the water-insoluble dyes such as chrome dyes, vat dyes, and sulfur dyes (Uygur 1997). It oxidizes the dyes by increasing the amount of oxygen in wastewater, thus reducing the COD at the same time. The intermediates resulting from such reactions are comparatively harmless and nontoxic as those obtained from chlorination and ozonolysis (Uygur 1997).

17.4.2.2 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) are highly sophisticated, novel methods, which hasten the oxidation and the degradation of a wide range of organic and inorganic substances, usually resistant to conventional treatment methods. In this technique the oxidizing agents such as ozone and hydrogen peroxide are usually used either in the presence of inorganic catalysts (Fe(II), Mn(II), and TiO_2) or in the presence or absence of irradiation source (Anjaneyulu et al. 2005). The primary oxidizing agents like O_3 and H_2O_2 produce in situ transitory species, mostly hydroxyl radicals that act as secondary oxidizing agents bringing about complete mineralization of the pollutants.

- *Oxidation with Fenton's Reagent*

One of the AOP combines both oxidation and coagulation by employing H_2O_2 in the presence of Fe(II) salts (Fenton's reagent). Hydroxyl radicals are generated from H_2O_2-based oxidation processes in presence ozone, UV light, inorganic salts such as Fe(II), Cu(II) (Uygur 1997) or ultrasound (Joshi and Purwar 2004). These radicals have a higher oxidation potential (2.80 V) as compared to hydrogen peroxide (1.78 V) and are more effective in destroying the organic molecules. Fenton's reagent is used for treating such wastewaters that are otherwise resistant to biological degradation. The use of this reagent for the treatment of dye effluent with or without coagulation, incineration, and biodegradation has been extensively explored (Uygur 1997; Xu et al. 2004). Xu et al. (Xu et al. 2004) reported the degradation of 20 dyes from different classes like acid, reactive, direct, cationic, disperse, and vat dye classes in aqueous solution by the oxidation process using Fenton's reagent. The generation of sludge through the flocculation of the reagent and the dye molecules and the requirement of acidic pH (Robinson et al. 2001) are the major disadvantages of using this reagent. The combination of UV radiation to Fenton's reagent results in the direct formation of hydroxyl radicals that greatly influences the decolorization of dyes. Studies by Xu et al. have shown that use of Fe(II)/H_2O_2/UV proved to be more efficacious in the oxidation of water-soluble as well as water-insoluble dyes in comparison with H_2O_2/UV and Fenton's reagent (Xu et al. 2004).

- *Photocatalytic Degradation*

Commercial dyes are synthesized in such a way so as to resist photodegradation; still a large number of catalysts and irradiation conditions have been explored for the effective decolorization of synthetic azo dyes. The rate of photodecomposition is enhanced by catalysts, and various literatures support the role of TiO_2 as an effective photocatalyst (dos Santos et al. 2007; Forgacs et al. 2004; Joshi and Purwar 2004). The chemical structure of the dye and presence of TiO_2 affect photodegradation of azo dyes under UV irradiation. In the photocatalytic decolorization/degradation of two important textile azo dyes, CI Acid Orange 7 and CI Direct Red 28, in the presence of UV and sunlight using TiO_2 as photocatalyst, the percentage decolorization obtained was 95% and 93%, respectively, after 2 hr. of photolysis (Kannan et al. 2006). The photocatalytic degradation of dyes is affected by several parameters like pH, catalyst, substrate concentration, and presence of electron acceptors such as hydrogen peroxide and ammonium persulfate and molecular oxygen (Konstantinou and Albanis 2004).

- *Photochemical Oxidation*

Photochemical oxidation employs the use of UV treatment coupled with H_2O_2 which not only cleave the large dye molecules to smaller fragments but also mineralize them to CO_2, water, and other inorganic oxides under suitable conditions (Yang et al. 1998). Hydroxyl radicals generated during the process bring about the decomposition of the dye molecules (Muruganandham and Swaminathan 2004). Presence of H_2O_2, intensity of radiation, pH, and dye structure are some of the factors on which the efficiency of this process depends (Espantaleon et al. 2003).

- *Ultrasonic Oxidation Processes*

Energy from the ultrasonic waves, when applied to the wastewater, causes physical and chemical changes through the generation and subsequent collapse of cavitation bubbles. In textile wastewater treatment, the cavitation bubbles act as a microreactor in which the pollutants are oxidized by the action of hydroxyl radicals (Yurtsever et al. 2015). The radicals are produced with the help of an energy source which can be acoustic, photolytic, or hydrodynamic in nature. Ultrasonic oxidation can be combined with other advanced oxidation processes (AOPs) such as sonolysis, sono-ozone process, sono-photocatalysis, sono-Fenton systems, and sonophoto-Fenton methods to increase the interaction between the dye molecules with the free radicals (Reddy et al. 2016).

17.4.2.3 Electrochemical Processes

Electrochemical techniques, like electrolysis, electrocoagulation, electroflocculation, etc., have been used to remove color, heavy metals, and suspended and dissolved solids from textile effluents. Moreover these methods are known to reduce the BOD and COD of wastewater (Joshi et al. 2004).

Electrolysis employs the use of an electrochemical cell, made up of fiber glass and iron electrodes. The wastewater that flows in between the electrodes acts as a medium through which the current passes from one electrode to another. Ferrous ions are generated at the positive sides of the electrodes, while at the negative sides, hydrogen gas and hydroxyl ions are generated due to the decomposition of water. The overall reactions give rise to hydrous iron oxide, ferrous hydroxide, and ferric oxyhydroxide (Joshi et al. 2004). Ferrous hydroxide helps in the removal of soluble and insoluble acid dyes from wastewater, and Fe(II) reduces azo dyes into aryl amines (Shah 2018). The electrochemical system can eliminate 90% of impurities. However, the process is expensive due to high energy requirements and uncontrolled radical reactions (Gill et al. 2002).

Electrocoagulation combines electrolytic reactions at electrodes and coagulation in wastewater effluents. It is an advanced multistep process for color removal. The pollutants, adsorbed on the coagulants, are separated by sedimentation. Current density and time of reaction play an important role in this technique. Iron or aluminum electrodes are usually used to continuously generate highly charged polymeric metal hydroxide species. These ions bearing opposite charges destabilize the colloids, thus coagulating them (Alkaya and Demirer 2014). This process has been well investigated as an alternative technology to chemical coagulation for treating textile and dyeing effluents in particular as no excess chemicals are used in this method (Bayramoglu et al. 2007).

17.4.3 Biological Methods

The problems associated with the conventional treatment methods of dye effluents have instigated researchers to opt for better alternatives. In view of this, biological methods of color removal is gaining interests recently owing to the following advantages: (1) environmental benignity, (2) being cost-effective, (3) production of less sludge, (4) yielding end products that are nontoxic or have complete mineralization, and (5) requiring less water consumption compared to physicochemical methods (Banat et al. 1996; Rai et al. 2005; Vitor and Corso 2008; Pajot et al. 2011). Bioremediation of these toxic compounds employ the usage of biological entities like plants and microbes. Biological treatment is generally considered to be the most effective way of removing wastes from wastewater enriched in organic constituents (Singh and Arora 2011). Bio-removal of dyes from wastewaters can be broadly categorized as aerobic treatment, anaerobic treatment, and combined anaerobic–aerobic treatment. Figure 17.2 shows the biological treatment methods, which are applicable for the treatment of textile wastewater.

17.4.3.1 Aerobic Treatment

In aerobic treatment, the microorganisms use the free oxygen dissolved in wastewater to degrade the organic compounds, and the end products are carbon dioxide and water. The dyes are xenobiotic compounds, recalcitrant in nature and generally resistant to oxidative biodegradation. The conventional aerobic treatment systems are stabilization ponds, aerated lagoons, trickling filters (packed bed reactors), and activated sludge. However aerobic degradation of dyes by microorganisms has been greatly studied (Adedayo et al. 2004; Cripps et al. 1990; Pajot et al. 2007; Senan and Abraham 2004). Activated sludge system is the mostly employed aerobic treatment

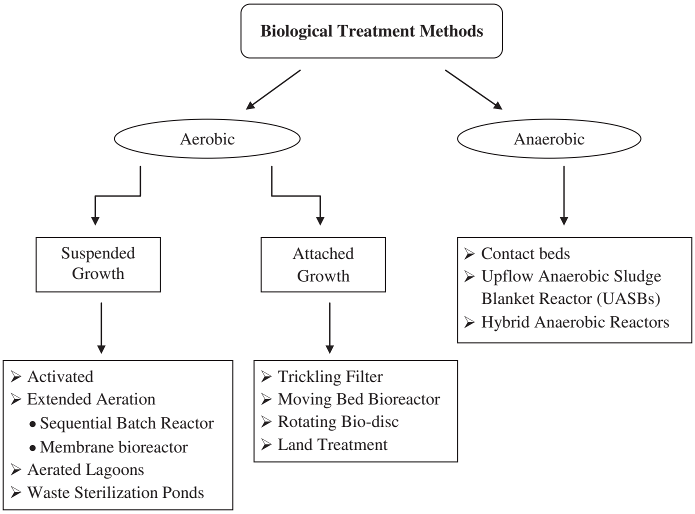


Fig. 17.2 Biological wastewater treatment methods (Ranade and Bhandari 2014]

system for dye effluents. In this process a large microbial population is suspended in aerated wastewater, subsequently generating significant amount of biological sludge. The cost of the process increases with the difficulty in the disposal of this sludge. Although biodegradable components of the effluent can be removed, complex substances like dyes show low removal rate due to lack of sufficient water solubility (Singh and Arora 2011). Among the synthetic dyes, disperse, direct, and basic dyes can be removed from wastewaters via adsorption onto activated sludge, whereas acid and reactive dyes remain largely unaffected due to low adsorption values. The factors which influence the adsorption of dyes on activated sludge are dye characteristics such as molecular structure and the number and position of the substituents in the dye molecule. Adsorption increases if the chromophores bear hydroxyl and nitro groups but decreases with the presence of sulfonate groups owing to the increased aqueous solubility of the dyes (Singh and Arora 2011).

Immobilized microbe reactors (IMBRs) increase the contact between the microbes and the waste, without producing excessive biosludge (Willmott et al. 1998). A larger fraction of microorganisms are available for waste degradation as they are attached to solid, porous matrix. The microbes inside the porous medium are protected from any kind of shock. The most common IMBRs include trickling filter, rotating biological contactor, and biotowers. Due to variation in the composition of waste inflow, the microbes fail to adapt themselves to the substrate which is a serious problem and reduces the efficiency of this treatment system. Thus, conventional aerobic systems are unsuccessful in degrading many dyestuffs and have to face many challenges like mechanical breakdown, excessive cost input, and production of large quantities of sludge.

17.4.3.2 Anaerobic Treatment

Anaerobic treatment is done in sealed tanks, and the end products obtained are methane and CO_2. Nitrogen- and sulfide-containing pollutants give rise to ammoniacal substances and H_2S. Anaerobic treatment is associated with significant heat generation. Methane and heat can be used for various energy-intensive purposes. Most of the anaerobic treatments reported to date have been conducted on azo dyes (Kim et al. 2008; Carliell et al. 1995). Dye structure as well as additional organic carbon sources influences the rate of decolorization (Senan and Abraham 2004).

Primary degradation and decolorization of the azo dyes under anaerobic environment involves the reductive cleavage of azo bond (Delée et al. 1998) with the subsequent generation of aromatic amines (Banat et al. 1996). The reductive cleavage is highly non-specific with respect to the organisms involved and the dyes selected. The reduction of the azo bond is overall a 4e − process, as depicted in the equation below: 2e − in reduction of azo bond to hydrazine link followed by another 2e − reduction process to the constituting amines (Singh and Arora 2011).

$$R^1 - N = N - R^2 \overset{2e^- + 2H^+}{\rightarrow} R^1 - NH - NH - R^2. \overset{2e^- + 2H^-}{\rightarrow} R^1NH_2 + R^2NH_2$$

The colorless amines generated are generally more toxic than the parent dye compounds and are resistant to further anaerobic degradation. The potential toxicity, mutagenicity, and carcinogenicity of these amines are well documented in literature (McMullan et al. 2001). These can be further completely mineralized by aerobic treatments (Méndez-Paz et al. 2005). Apart from the production of biogas, other advantages of the anaerobic treatment include requirement of less space, low running costs, and production of less sludge.

Decolorization of various azo dyes via reduction of the azo bond by mixed aerobic and facultative anaerobic microbial consortia under anoxic conditions has been reported (Khehra et al. 2005; Beydilli et al. 2000; Nigam et al. 1996). Azo dye decolorization under anoxic conditions is also non-specific and requires yeast extract or peptone (Nigam et al. 1996). Kalme et al. reported that a *Pseudomonas* species was able to biodegrade benzidine-based dye CI Direct Blue 6 completely with 88.95% of COD reduction under static and anoxic conditions (Kalme et al. 2007). The effect of additional carbon sources for anoxic decolorization by facultative anaerobes and fermenting bacteria depends on the bacterial species employed. It was observed that glucose enhanced the decolorization of CI Mordant Yellow 3 by *Sphingomonas xenophaga*, whereas decolorization of CI Reactive Red 22 by *Pseudomonas luteola* decreased in the presence of glucose (Chang et al. 2001).

17.4.3.3 Sequential Anaerobic–Aerobic Treatment

Decolorization of azo dyes mostly occurs through the reductive cleavage of the azo bonds under anaerobic conditions resulting in aromatic amines. These toxic amines are resistant to further degradation under anaerobic condition but can be mineralized aerobically. This makes coupled anaerobic–aerobic treatment a complete setup for remediating these azo dyes.

In a study involving the decolorization of the diazo dye CI Reactive Black 5, up to 98% decolorization was obtained under anaerobic condition, using a sequential anaerobic–aerobic system. Partially granulated sludge culture with co-substrate glucose was used, and the intermediates were mineralized aerobically (Sponza and Işik 2002). Different sulfonated dyes like CI Acid Orange 10, CI Acid Black 1, CI Direct Red 2, and CI Direct Red 28 have also been treated in the same manner using glucose as a co-substrate, and the studies showed that the amines resulted got completely mineralized in a subsequent aerobic treatment (Rajaguru et al. 2000).

Studies on simulated textile wastewater containing reactive azo dye CI Reactive Red 141 using coupled anaerobic–aerobic system have also been reported (O’Neill et al. 2000). The intermediates formed were aromatic amine derivatives having additional groups such as –OH and –SO3 which further degraded into more polar, nonaromatic by-products after the aerobic treatment.

Combined anaerobic–aerobic system has also been used to treat textile wastewaters containing both water-soluble and water-insoluble dyes such as reactive, disperse, and vat dyes, anthraquinones, and indigoids (Frijters et al. 2006). The effluent was decolorized anaerobically, while after sequential anaerobic–aerobic treatment, it showed no toxicity. When the anaerobic step was partially bypassed, the effluent showed increased toxicity and decreased color removal indicating the importance of anaerobic treatment step in decolorizing and detoxifying the textile wastewater in the sequential anaerobic–aerobic system. One of the major

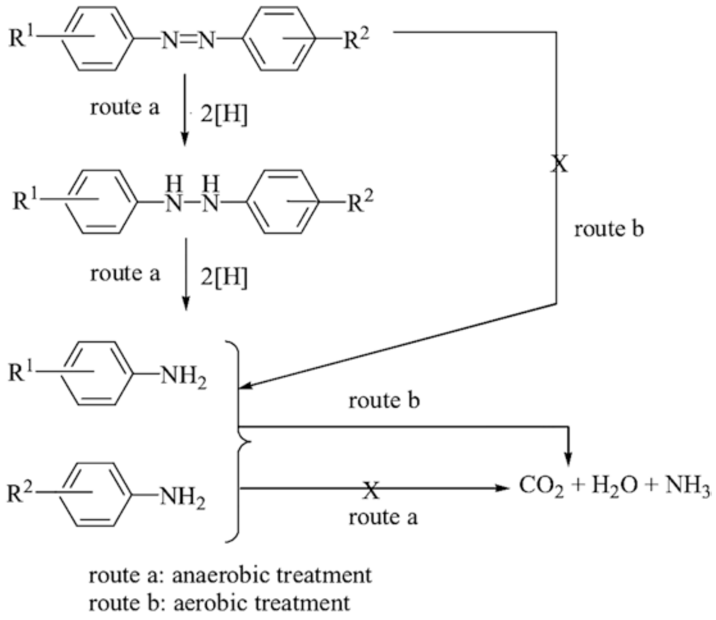


Fig. 17.3 General overview of the fate of azo dyes and aromatic amines during simultaneous anaerobic–aerobic treatment (Singh and Arora 2011)

disadvantages of this strategy is the autoxidation of aromatic amines, which are unstable under aerobic conditions which is a serious problem if complete mineralization of the azo dye was the priority of the treatment system (Fig. 17.3).

17.4.3.4 Decolorization and Degradation of Azo Dyes by Plants (Phytoremediation)

Plants hold great promise for the remediation of soils and groundwater contaminated with heavy metals and organic pollutants (Patil et al. 2009). The main advantages of phytoremediation include (1) effective and inexpensive approach, (2) availability of large biomass that requires little nutrient input, (3) being easy to handle, and (4) environmental sustainability (Ghodake et al. 2009; Kagalkar et al. 2009).

Studies by Mbuligwe et al. showed color reduction up to 77% in wetlands which consisted of coco yam plants (Mbuligwe 2005). Three plant species, *Brassica juncea*, *Sorghum vulgare*, and *Phaseolus mungo*, have been employed for the decolorization of the reactive group of azo dyes and textile effluent, when decolorization of up to 79, 57, and 53%, respectively, was achieved (Ghodake et al. 2009). Patil et al. (2009) determined the enzyme machinery of root cultures of *Tagetes patula* L. (marigold) responsible for decolorization of Reactive Red 198. Kagalkar et al. reported the degradation of textile dye Reactive Red 5B by *Blumea malcommi* (Kagalkar et al. 2009). The decolorization of two textile dyes, namely, Yellow 5G and Brown R, has been studied using fast-growing plant species *Parthenium hysterophorus*, *Alternanthera sessilis*, and *Jatropha curcas* (Shinde et al. 2012).

Phytoremediation of textile wastewater using *Phragmites australis* showed promising results (Carias et al. 2007).

Though phytoremediation is considered a greener alternative for degradation of toxic compounds, it has its share of drawbacks which include problems in large-scale application because of sensitivity of plants to toxic substances. Different plants have their own tolerance limit for various pollutants which often restricts their usage. Moreover requirement of large areas for implementation of the treatment, evapotranspiration of volatile organic pollutants, and bioavailable fraction of the contaminants pose as obstacles in this approach (Ghodake et al. 2009). Extensive research in the field of phytoremediation is required as the details of plant metabolic pathways used in decomposition of the contaminants are yet to be fully understood (Chaudhry et al. 2005) which in turn restricts the widespread application of plants for the said technique.

17.4.3.5 Decolorization and Degradation of Azo Dyes by Microbes

Bioremediation or the use of microbes to remediate pollution is one of the prominent research areas in environmental sciences. New resistant strains developed as the microbes get adjusted to the harmful wastes, and these new strains are capable of transforming the toxic chemicals into less harmful forms. The viability of microbial decolorization depends on the adaptability and the activity of the selected microorganisms. Thus, a large number of species have been tested for their capability of decolorizing and mineralizing various dyes in recent years (Pandey et al. 2007). The screening and isolation of potent species and subsequent degradation of compounds by them are one of the key features of biological aspect of effluent treatment (Chen et al. 2008). A wide variety of microorganisms are capable of decolorizing of a wide range of dyes including bacteria (Dawkar et al. 2008; Jadhav et al. 2008; Kalyani et al. 2009; Saratale et al. 2009c; Telke et al. 2008), fungi (Fournier et al. 2004; Humnabadkar et al. 2008; Saratale et al. 2006), yeasts (Jadhav et al. 2007; Lucas et al. 2006; Saratale et al. 2009a), actinomycetes (Machado et al. 2006), algae (Acuner and Dilek 2004; Daeshwar et al. 2007; Parikh and Madamwar 2005), and plants (phytoremediation) (Aubert and Schwitzguebel 2004; Ghodake et al. 2009; Kagalkar et al. 2009). Often mixed culture or bacterial consortia are used in place of pure cultures to obtain better results (Ghanem et al. 2012). Mixed fungal cultures (Nascimento et al. 2011) and fungal–bacterial consortia (Lade et al. 2012) have also been exploited for decolorization studies. Microbial bioremediation can occur via two principal mechanisms: biosorption and enzymatic degradation (Singh and Singh 2017).

- *Biosorption*

The uptake or accumulation of hazardous chemicals by microbial mass has been termed as biosorption (Kumar et al. 1998). The biomass of different microorganisms like bacteria, filamentous fungi, yeast, and algae have been used to accumulate dyes from the industrial effluents (Bhatnagar and Sillanpaa 2010). In the past few years, researchers have tried to use fungal and yeast cells (Kalaiarasi et al. 2012), bacterial biomass (Han and Yun 2007), and algal biomass (Khataee et al. 2013) to treat textile effluents as they are cost-effective and include minimal processing steps (Vitor and Corso 2008). The cell wall components of these microorganisms such as heteropolysaccharides and lipids, consisting of different functional groups like amino, hydroxyl, carboxyl, phosphate, etc., generate strong attractive forces between the azo dye and cell wall (Srinivasan and Viraraghavan 2010; Das and Charumathi 2012). The effectiveness of biosorption is influenced by factors like pH, temperature, ionic strength, time of contact, adsorbent, dye concentration, dye structure, and selection of microorganism (Renganathan et al. 2006; Vijayaraghavan and Yun 2007; Erden et al. 2011; Ambrosio et al. 2012). Algal biomass are being considered as potential biosorbents as they can be found in both fresh and salt water (Wu and Jean 2012). The biosorption capacity of algae is attributed to their relative high surface area and high binding affinity (Donmez and Asku 2002). The physical processes responsible for biosorption by algae are electrostatic attraction and complexation in the cell wall of algae (Satiroglu et al. 2002). Dead algal cells are considered to be advantageous over live ones as no nutrients are required to maintain them (Daneshvar et al. 2012). They can be stored and used for a long time. Moreover they can be regenerated using organic solvents or surfactants (Fu and Viraraghavan 2001). The process of biosorption is highly selective and economic and can perform at low concentration (Hammaini et al. 2002), but the disadvantage of this method is that the biosorbent easily gets saturated.

- *Enzymatic Degradation*

Microbial biodegradation of toxic chemicals is usually brought about the action of bio-transforming enzymes of the microorganisms (Saratale et al. 2007a). Microorganisms such as bacteria, algae, fungi, yeast, etc. and their enzymes can be used in removing the color of different azo dyes through anaerobic, aerobic, or sequential anaerobic–aerobic treatments. Several studies report the degradation of complex organic substances by microbial enzymes, such as laccase (Hatvani and Mecs 2001), lignin peroxidase (Duran and Esposito 2000), NADH–DCIP reductase (Bhosale et al. 2006), tyrosinase (Zhang and Flurkey 1997), hexane oxidase (Saratale et al. 2007b), and aminopyrine N-demethylase (Salokhe and Govindwar 2003). Microbial enzymes that are responsible for dye decolorization can be categorized as reductive and oxidative enzymes.

Azoreductases are the primary reductive enzymes, produced by microorganisms such as bacteria (Misal et al. 2011), algae (El-Sheekh et al. 2009), and yeast (Vitor and Corso 2008). They function by cleaving the azo bond and generating of toxic colorless aromatic amines under reduced conditions (Pandey et al. 2007). These non-specific, cytoplasmic enzymes are NADPH, NADH, and FADH-dependent enzymes. On the basis of reducing equivalent used to reduce azo linkages, enzymes have been identified as FMN-dependent reductases (Burger and Stolz 2010), FMN-independent reductases (Burger and Stolz 2010), NADH-dependent reductases (Misal et al. 2011), NADPH-dependent reductases (Mendes et al. 2011), and NADH–DCIP reductases (Phugare et al. 2010).

The oxidative enzymes include manganese peroxidase (MnP), lignin peroxidase (LiP), laccase (Lac), tyrosinase (Tyr), etc. (Martorell et al. 2012). The removal of toxic compounds from waste by these enzymes takes place through the formation of free radical followed by insoluble product (Torres et al. 2003). Peroxidase is a heme-containing enzyme and widely distributed in plants, microorganisms, and animals (Duarte-Vazquez et al. 2003). The function of plant horseradish peroxidase and LiP from *Penicillium chrysosporium* in the oxidation of Methylene Blue (Basic Blue 9) and Azure B dyes has been reported by Ferreira-Leitao et al. (2007). Laccases are multi-copper oxidases, and removal of dyes by them is ascribed to their distinct features like non-specific oxidation capacity, no requirement for cofactors, and not using of readily available oxygen as an electron acceptor (Telke et al. 2011). They mediate the decolorization of textile dyes either by direct oxidation or via indirect oxidation by using redox mediators (e.g., ABTS) (Khlifi et al. 2010).

- *Decolorization and Degradation of Azo Dyes by Fungi*

Filamentous fungi occupy a wide range of ecological niches such as soil, living plants, and organic waste, and their survival is maintained by their rapid adaptation of their metabolism to varying carbon and nitrogen sources. They produce a large number of intra- and extracellular enzymes capable of degrading various complex organic pollutants such as polyaromatic hydrocarbons, organic waste, dye effluents, and steroid compounds (Gadd 2001; Humnabadkar et al. 2008; McMullan et al. 2001; Saratale et al. 2007a, b). The lignolytic fungal enzymes like lignin peroxidase (LiP), manganese peroxidase (MnP), and laccase are non-specific in nature (Christian et al. 2005). Most studies on the azo dye biodegradation have focused on fungal cultures from white rot fungi (Machado et al. 2006). The mostly studied white rot fungi with respect to dye degradation is *Phanerochaete chrysosporium*, but long growth cycle and the requirement for nitrogen-limiting conditions are some of the disadvantages of this species. Moreover their absence in wastewater renders the production of their enzymes unreliable (Robinson et al. 2001). The long hydraulic retention time required for complete decolorization also restricts the efficacy of fungal decolorization system (Banat et al. 1996; Chang et al. 2004), and the preservation of fungi in bioreactors is also a matter of concern (Stolz 2001).

- *Decolorization and Degradation of Azo Dyes by Yeast*

Yeasts have mostly been employed for biosorption, enzymatic degradation, or a combination of both (Yu and Wen 2005). Some yeast species, such as *Candida albicans* (Vitor and Corso 2008), *Candida tropicalis* (Yang et al. 2003), *Debaryomyces polymorphus* (Yang et al. 2003), and *Issatchenkia occidentalis* (Ramalho et al. 2004), have been used for enzymatic biodegradation and consequent decolorization of different azo dyes. These are fast multiplying like bacteria and can withstand extreme environmental conditions (Yu and Wen 2005). Low pH has been found to be favorable for the degradation of azo dyes by yeast species. *Saccharomyces cerevisiae* MTCC-463 was reported to have a role in the decolorization of Malachite

Green and Methyl Red (Jadhav and Govindwar 2006; Jadhav et al. 2007). Saratale et al. (2009a) reported the decolorization of Navy Blue HER by using *Trichosporon beigelii* NCIM-3326, and the enzymatic pathway along with the toxicity of the by-products was also studied. *Candida oleophila* (Lucas et al. 2006) was found to decolorize the diazo dye Reactive Black 5 with satisfactory results.

- *Decolorization and Degradation of Azo Dyes by Algae*

Cyanobacteria and algae are photosynthetic organisms, and they are ubiquitously distributed in a wide range of habitats, thus are gaining interests in wastewater remediation. Studies report that algae degrade azo dyes through an induced form of an azoreductase (Vijayaraghavan and Yun 2007). Algae bring about decolorization by incorporation and simultaneous utilization of chromophores for biomass production, conversion of colored molecules to colorless forms, and adsorption of chromophores on algal biomass (Saratale et al. 2011). Several species of *Chlorella* and *Oscillatoria* were found to be successful in transforming the toxic aromatic amines, produced due to the reductive cleavage of the azo bond, into simpler metabolic intermediates like CO_2 and water (Acuner and Dilek 2004). The decolorization by algae is ascribed to biosorption followed by bioconversion and biocoagulation (Mohan et al. 2002).

- *Decolorization and Degradation of Azo Dyes by Bacterial Monoculture and Consortia*

The bacterial decolorization of azo dyes mostly occurs under anaerobic, facultative anaerobic, and aerobic conditions. Under anaerobic condition the azo bonds undergo reductive cleavage resulting in toxic aromatic amines by the action of azoreductase enzymes. The amines are further degraded in the subsequent aerobic step (Joshi et al. 2008). Extensive studies have been carried out to determine the role of the diverse groups of bacteria in the decolorization of azo dyes (Pandey et al. 2007). The bacterial decolorization and degradation of these dyes has been in focus since it can achieve a higher degree of biodegradation and mineralization in less time as compared to other microbes and is applicable to a wide variety of azo dyes (Saratale et al. 2009c.). Efforts to isolate pure bacterial cultures capable of degrading azo dyes started in the 1970s. *Bacillus subtilis*, *Aeromonas hydrophila*, and *Bacillus cereus* were first reported for dye degrading activity (Wuhrmann et al. 1980).

Often bacterial consortia have been found to be more effective than individual pure strain (Nigam et al. 1996). In a microbial consortium, the individual strains may attack the dye molecule at different positions or may utilize metabolites produced by the coexisting strains for further decomposition (Chang et al. 2004; Saratale et al. 2009b). However reproducing results with mixed cultures is a problem, and it indicates a gross effect. The extent of functioning of individual strain is difficult to predict. Interpretation of experimental results as well as determination of enzymatic pathways involved in dye degradation becomes easier with individual cultures. Once the enzymatic machinery is known, it can be regulated using tools of molecular biology and biochemistry for enhanced degradation of the dyes by the modified strains of bacteria.

- *Bacterial Degradation of Azo Dyes by Immobilized Cells*

Recently, the bacterial cells have been immobilized, either by attachment or entrapment method, and employed in dye degradation studies. These cells are found to be more stable and tolerant toward the environmental changes like temperature, pH, concentration of pollutants, etc. than the free ones. Moreover these can be reused and high density can be maintained in a continuous reactor. Immobilization has been carried out using various carriers like nylon web, polyurethane foam, activated carbon, pine wood, sodium alginate, agar, and porous polystyrene. Several common species of bacteria, like *Enterobacter* sp., *Pseudomonas* sp., and *Morganella* sp., have been immobilized on kaolin, bentonite, and powdered activated carbon (PAC), respectively, and their degradation efficiency was studied using various azo dyes (Barragan et al. 2007). Immobilized cells of *A. hydrophila*, *C. testosterone*, and *A. baumannii* have been used in a reactor for the degradation of azo dye Red RBN (Chen et al. 2003). An anaerobic environment is created when bacterial cells are immobilized by entrapment method which helps in the reductive cleave of the azo bonds. Immobilized cells of bacteria on furnace charcoal in downflow fixed film bioreactor have been used in treating industrial dye effluents (Sheth and Dave 2010).

- *Bacterial Degradation of Azo Dyes by Microbial Fuel Cells (MFCs)*

A microbial fuel cell is a bioelectrochemical system that converts chemical energy to electrical energy through the interaction of microbes with electrodes mediated by electrons that are either removed or supplied through an electrical circuit (Rabaey et al. 2006). MFCs are gaining huge interest in the recent years as wastewater can be used as its substrate, which automatically favors sanitization of the same. It thus saves the running costs of wastewater treatment plants (Lu et al. 2009). Decolorization of azo dye Active Brilliant Red X3 has been studied using MFCs which showed satisfactory results along with generation of electricity (Sun et al. 2009). MFCs thus hold great promise in effluent treatment with the simultaneous production of bioenergy to meet the increasing energy needs of the modern world.

17.5 Hybrid Technologies for Efficient Dye Removal

Literature survey suggests that over the past few decades, almost every possible treatment methods for color removal from effluents have been over exhausted, yet none could prove to be the ultimate one. Even if some are completely successful in even mineralizing the synthetic dyes in the wastewater effluents and generate water for reuse, they were often found to be economically not feasible for scale-up

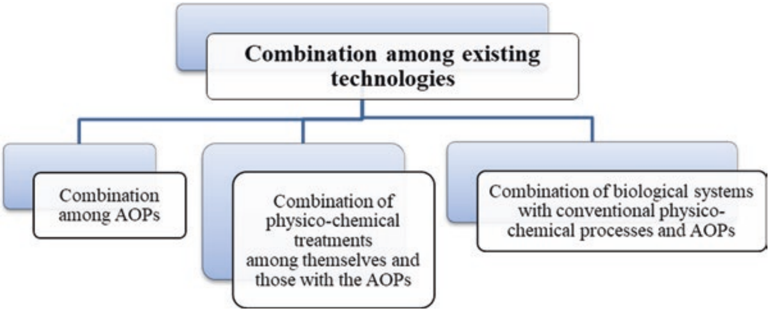


Fig. 17.4 Hybrid technologies for dye removal

procedures. Some methods, in spite of being cost-effective, may not be efficacious. Thus recent works mostly adhere to the combination of processes for enhanced decolorization and degradation while always keep in focus on the cost investment and industrial scale-up. The combination of different processes can be broadly categorized as shown in the figure below (Fig. 17.4).

17.5.1 Combination Among AOPs

Although advanced oxidation processes (AOPs) have been deeply researched upon, still due to some drawbacks, commercialization of the processes has not been possible. These are cost intensive and sophisticated, thus effective for wastewater with very low concentrations of organic dyes. The efficiency of these processes is further reduced due to the presence of additional impurities, salts, synthetic precursors, and dispersing agents in commercial dyebath (Alaton 2003). AOPs generate free radicals which bring about the degradation, so combination among different AOPs is expected to give rise to more free radicals, thus enhancing the function (Gogate and Pandit 2004a, b I and II). Again, the drawbacks of the individual AOPs may be eliminated by the characteristics of the other ones. The cost/energy efficiency of the combined processes will be determined by operating conditions and the type of the effluent.

17.5.1.1 Combination Among Different Photochemical Processes

The photochemical reactions generate free radicals by the interaction of photons with the chemical species present in the effluent. Studies have reported radicals generated through UV radiation, and simultaneous photochemical degradation of oxidizing compounds like hydrogen peroxide (Aleboyeh et al. 2003), ozone (Chen et al. 2002), or Fenton's reagent (Neamtu et al. 2002) has been considered to be superior to individual UV radiation or sole utilization of such oxidants. A pretreatment of effluents, containing high UV-absorbing components, by ozonation leads to the removal of the said components which speeds up the H_2O_2–UV posttreatment by increasing UV penetration (Alaton and Balcioglu 2001).

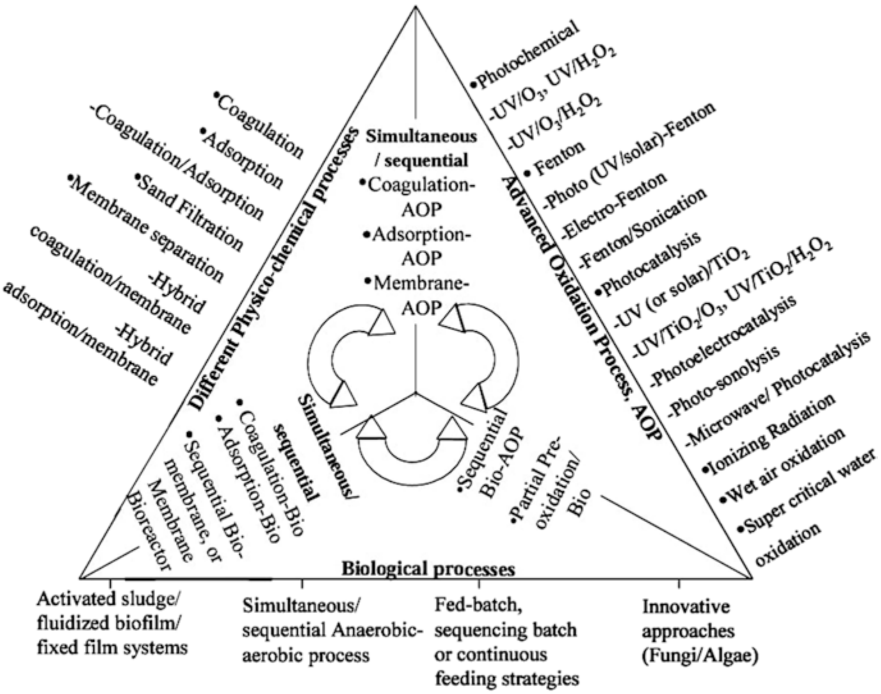


Fig. 17.5 Simplified representation, highlighting the combinations among different existing processes for efficient color removal from dye effluents (Hai et al. 2007)

Photocatalytic oxidation is another phenomenon that generates free radicals by the interaction with the surface of semiconductors. Various chalcogenides (oxides such as TiO_2, ZnO, ZrO_2, CeO_2, etc. or sulfides such as CdS, ZnS, etc.) have been used as photocatalysts in different experiments. TiO_2 is extensively used as it is comparatively inexpensive, nontoxic, insoluble, resistant to photocorrosion, and biologically immune (An et al. 2002). However drawbacks of photocatalysis include scouring of films comprising immobilized powders of catalyst and reduced surface to volume ratio of the catalysts. Reports on utilization of photocatalysis in presence of O_3 (Moraes et al. 2002) or H_2O_2 (Sugiarto et al. 2002) indicated enhanced rate of decoloration and mineralization (Fig. 17.5).

Modifications of Fenton processes like photo-Fenton reaction using Fe(II)/Fe(III) oxalate ion, H_2O_2, and UV light have gained huge interests as means for decolorization of synthetic dyes (Shah et al. 2003; Swaminathan et al. 2003), as in this technique H_2O_2 is utilized more rapidly by three simultaneous reactions, namely, direct Fenton action, photoreduction of Fe(III) ions to Fe(II), and H_2O_2 photolysis. As a result more hydroxyl radicals are generated in comparison with the conventional Fenton method or the photolysis (Bandara et al. 1996; Gogate and Pandit 2004a, b I). H_2O_2 oxidation process using β-FeOOH as a catalyst can function over a broad range of pH (4–8) as compared to conventional Fenton's reagent.

17.5.1.2 Combination Between Photochemical/Electrochemical Processes

Often electrochemical methods and photocatalysis have been combined for enhanced decoloration and COD removal (An et al. 2002), and this hybrid process is unaffected by the presence of salt in solution which otherwise is harmful for sole photocatalysis (Zhang et al. 2003). Another example is electro-Fenton process that requires only catalytic quantity of Fe^{+2} as H_2O_2 is produced in situ; thus transport of this hazardous oxidant can be avoided (Guivarch et al. 2003; Nicolet and Rott 1999).

17.5.1.3 Combination Among Sonolysis and Other AOPs

Within a solution, local sites of high temperature and pressure for short span of time result due to acoustic cavitation due to ultrasound vibration, which gives rise to H_2O sonolysis with the simultaneous production of radicals and direct or indirect destruction of the solutes via the free radicals. Since only sonolysis is unable to completely mineralize the complex organic and inorganic pollutants of the wastewater, it is combined with AOPs for better results. Sonolysis when combined with photochemical oxidation can prevent severe mass transfer limitation and eliminate other drawbacks of the individual sonolysis process (Mrowetz et al. 2003). Sonification, by increasing the oxygen uptake and transfer, has been found to enhance the oxidation efficiency of UV/H_2O_2 (Fung et al. 1999; Fung et al. 2001). Studies have reported that electrooxidation of dyes is enhanced by simultaneous sonolysis (Lorimer et al. 2000).

17.5.2 Combination Among AOPs and Other Physicochemical Processes

The already established physicochemical processes when combined with the recent treatment methods like advanced oxidation processes offer lucrative outcomes.

17.5.2.1 Coagulation-Based Combinations

Coagulation/flocculation/precipitation processes have been often used as a pretreatment of raw wastewater before its discharge to treatment plants and have been found to successfully reduce the amount of COD, but in the context of color removal, they are quite ineffective (Hao et al. 2000; Kim et al. 2004a, b, c). Water-soluble dyes are difficult to remove by conventional coagulants, and there is simultaneous production of sludge (Robinson et al. 2001). Recently a new highly stable coagulant, polyaluminium ferric chloride (PAFC), has been reported which is applicable for both water-soluble and water-insoluble dyes (Gao et al. 2001).

Studies show that coagulation with subsequent adsorption produces effluent that can be reused and reduce the consumption of coagulant by 50%, thus automatically decreasing the formation of sludge (Papic et al. 2004). Simultaneous application of coagulation and Fenton oxidation has proved to be efficacious over their standalone applications (Kim et al. 2004a, b, c).

Chemical coagulation when used as a posttreatment for Fenton's oxidation reduced the floc-settling time, enhanced the rate of decoloration, and reduced soluble iron in the effluent (Lin and Lo 1997). When the processes are applied in the reverse order, complete decoloration with better COD removal was observed, with the added advantage of reduction of load on the AOP, thereby reducing chemical usage (Balcıoğlu et al. 2003).

17.5.2.2 Adsorption-Based Combinations

Carbon-based compounds offer excellent adsorption properties and are widely used for the removal of dyes from industrial effluents (Forgacs et al. 2004). Activated carbon (powdered or granulated) is the most exploited adsorbent, but its cost and inevitable weight loss during regeneration are the major obstacles for its widespread usage. As a result low-cost sorbents like agricultural and industrial by-products, chitosan, zeolite, clay, fly ash, coal, agricultural wastes, and lignocellulosic wastes are being experimented upon for dye removal (Babel and Kurniwan 2003; Naim and El Abd 2002). However, adsorption is physical phenomena involving only phase change of pollutants, without their degradation. Moreover these sorbents are non-regenerable with the added drawback of sludge disposal problem (Abu-Salah et al. 1996). Thus it is profitable to combine adsorption with processes which can regenerate the sorbent after the subsequent separation and mineralization of the concentrated pollutants. The contaminants thus separated may be degraded by wet air oxidation (Shende and Mahajani 2002; Wu et al. 2004). In case of application of partial degradation for the regeneration of the adsorbent, the residual wastewater can be conveniently taken care of by applying some AOPs.

17.5.2.3 Membrane-Based Combinations

Membrane technology has been in use for concentrating dyestuffs and other contaminants from the effluents, but sludge production and frequent membrane fouling require the replacement of the costly membranes which is a major disadvantage of this technique (Chakraborty et al. 2003). Recent studies thus focus either on coupling of membrane separation with other technologies or on the reduction of the membrane-concentrate disposal problem. Combination of membrane separation and photocatalysis has reported the eradication of the problem associated with the separation of ultrafine catalyst from the treated liquid in case of slurry reactors. Membranes can act as the support for photocatalyst in case of immobilized catalysis (Molinari et al. 2004). Studies suggest that a photooxidative (UV/TiO_2/H_2O_2) pretreatment followed by membrane filtration leads to the partial breakdown of the high molecular weight compounds responsible for membrane fouling (Tay et al. 2001). The smaller fragments generated can still be concentrated by the membrane, without affecting the charge of the membrane surface. Reusable water can be obtained with the added advantage of alleviating the chance of membrane fouling, when membrane separation (UF/NF) is used as a posttreatment of coagulation/flocculation (Bes-Pía et al. 2002; Bes-Piá et al. 2003).

17.5.3 Biological Treatment-Based Combinations

For devising hybrid technologies, combining biological treatment methods with other established ones like AOPs or different physicochemical ones is gaining tremendous significance because of the wide array of advantages of bioremediation as discussed in Sect. 17.4.3.

17.5.3.1 Combination Among Biological Processes

Numerous biological treatments including activated sludge, fluidized biofilm (Yung-Kyu and Chul-Hee 1996), different fixed film systems (Ahn et al. 1999), or combinations thereof (Zaoyan et al. 1992) have formed the basis of different experimental studies. Although the azo dyes are resistant to aerobic degradation, their co-metabolic reductive cleavage with the concurrent exploitation as the only source of carbon and energy (leading to mineralization) has been reported. Sequential anaerobic–aerobic treatment is often applied for azo dyes as already discussed in Sect. 17.4.3.3. Different combinations among biological processes include simultaneous anaerobic–aerobic process (microbial immobilization on a matrix providing oxygen gradient; Kudlich et al. 1996) or an anaerobic–aerobic hybrid reactor (Kalyuzhnyi and Sklyar 2000), anoxic plus anaerobic–aerobic process (Panswad et al. 2001), anaerobic/oxic system (An et al. 1996), aerobic (cell growth)/anaerobic (decolorization) system (Chang and Lin 2000), etc. All these methods involve fed-batch, sequencing batch, or continuous feeding strategies and yielded satisfactory results.

The advantages associated with the biological treatment techniques have led the researchers to focus on reducing the intrinsic limitations of these methods. Some inventive endeavors consist of two-stage activated sludge process (high-load first stage for biosorption and negligible decomposition of high molecular organic compounds, followed by a low-load polishing stage) (Knudsen et al. 1994); two-phase anaerobic treatment where the acidic phase bioreactor is also exploited for textile production (Feitkenhauer and Meyer 2001); activated sludge pretreatment for decreasing the organic nitrogen load, before decolorization by suitable fungal species (Miyata et al. 2000); sequential fungal and anaerobic treatment (Feijoo et al. 1995); coupled fungal biofilm and activated sludge treatment for decoloration (Kapdan and Kargi 2002); bioreactor with algal–bacterial consortia (Aziz and Ng 1993), etc.

17.5.3.2 Combination Among Biological and Other Physicochemical Processes/AOPs

Among the different physicochemical processes, coagulation is mostly used with bioremoval of color either as a pre- (Yung-Kyu and Chul-Hee 1996) or post-treatment (Dulkadiroglu et al. 2002), the choice of which is governed by the dose of the coagulant, quantity of sludge, and amount of non-biodegradable substances present in wastewater. For alkaline wastewaters, coagulation as a pretreatment to biological one may be advantageous, as after biological treatment neutral pH restricts the further use of ferrous sulfate. When coagulation is preceded by biological treatment, the amount of coagulant required is found to be less; also there is decreased production of chemical sludge (Dulkadiroglu et al. 2002; Grau 1991). Often biological treatment is applied at the first (Kim et al. 2002), intermediate (Ahn et al. 1999), or last stage (Lin and Peng 1996) of a three-step treatment plan comprising of certain physicochemical process and AOPs. Biological pretreatment requires specially screened and adapted microbes that can effectively degrade the dye molecules. On the other hand, treating dye wastewater by physicochemical methods/AOPs before biological treatment is often seen as a suitable option because of the recalcitrant nature of most of the dyes and other toxic chemicals present in the effluent. The choice and the order in which different physicochemical process and AOPs should be used for treating dye wastewater is influenced by the characteristics of the effluent and governed by the type of toxic substances to be eliminated from the wastewater. For instance, using AOPs as a primary treatment for effluents containing huge amount of suspended or colloidal solids is not a rational choice as these are very sophisticated methods as well as cost intensive. In that case different physicochemical methods can be employed as a pretreatment for their removal (Ciardelli and Ranieri 2001; Kim et al. 2002). On the other hand, after ozonation (Lin and Lin 1993) or electroflocculation (Ciardelli and Ranieri 2001; Kim et al. 2002), enhanced COD removal can be achieved by the subsequent application of different physicochemical treatments. In order to obtain reusable water, AOPs and other physicochemical methods can be used as a subsequent step in the treatment of wastewater after biological pretreatment.

In the pursuit of finding more efficient ways of color removal, nowadays the existing methods are being used in an integrated fashion which can be seen as a modification over the processes designed to have stepwise pre- and posttreatment measures for dye effluents. This is quite an innovative approach in which the synergistic effect of the processes increases the efficacy of the color removal (Lopez et al. 1999). A common example is the simultaneous use of advanced oxidation with activated sludge treatment. The AOP is particularly employed for the conversion of the recalcitrant substances to biodegradable by-products, thereby reducing the cost of complete mineralization by the AOPs. Existing literature reflects that different AOPs like partial oxidation by ozonation (Chen et al. 2002), H_2O_2 (Cisneros et al. 2002), photocatalysis (Reyes et al. 1998), photo (solar)-fenton (Torrades et al. 2004), wet air oxidation (Pintar et al. 2004), combined photocatalysis and ozonation/H_2O_2 (Moraes et al. 2002; Sugiarto et al. 2002), photoelectrochemical process (An et al. 1996), sub- and supercritical water oxidation (Kim et al. 2004a, b, c), and electron-beam treatment (Han et al. 2004) have been employed in the partial pre-oxidation of dye effluents in the recent years. The selection of the specific AOP for the pre-oxidation process, based on their characteristics, is a crucial step in designing the integrated process as it increases the efficiency of the biological treatment. A step-by-step approach for choosing the proper chemical pretreatment for the integrated process has been well documented in literature (Mantzavinos and Psillakis 2004). The duration of pre-oxidative treatment should be less unless necessary; otherwise low molecular weight biodegradable substances are also mineralized, thus increasing the overall cost of the process (Jochimsen et al.

1997). If the dye wastewater contains large fractions of biodegradable substances, it is not wise to opt for AOPs for pre-oxidation as it will only lead to the excess consumption of chemicals without any enhancement in biodegradability. In such cases, AOPs should be antecedent to a biological pretreatment (Hörsch et al. 2003; Vidal et al. 2004).

Bioremediation is often coupled with adsorption, as the substances present in the dye wastewater are not readily biodegradable in nature. For this very reason, some studies report the addition of biosorbents like activated carbon into activated sludge systems (Abu-Salah et al. 1996). The adsorbent readily adsorbs the harmful substances leaving behind a free fraction to be metabolized by the suitable microbes at the liquid–solid surface. Biogeneration of activated carbon has been reported earlier by the extracellular enzymatic degradation of the toxic adsorbed chemicals (Specchia and Gianetto 1984; Xiaojian et al. 1991). This combined process is a single-step approach to remove color as well as COD from the dye effluents (Márquez and Costa 1997). Activated carbon, by virtue of quinone group present in its structure, acts as a redox mediator, thus helping in the reduction of azo dyes (Zee et al. 2003). However, one of the disadvantages of this coupled system is that high biomass concentration (> 3 g/l) often leads to the entrapment of the carbon particles into the floc matrix. This causes the carbon particles to lose their adsorption capacity; also it has an inhibitory effect on the growth of the microbes and subsequent removal of the dyes. Existing literature is suggestive of different innovative combinations of biodegradation and adsorption. Fluidized bed reactor along with complex pellets of white rot fungus and activated carbon showed better results in comparison with the individual application of the said constituents in dye removal (Zhang and Yu 2000). Application of fixed granular activated carbon (GAC) bed with suitable bacteria, capable of cleaving the chromophoric bond and aromatic rings, showed superior results than conventional GAC bed (Walker and Weatherley 1997). However, it is very important to maintain the DO level in GAC for stable microbial activity, COD and color removal, and prolonged carbon bed life (Qing et al. 2004).

The main purpose of remediation of effluents is the removal of hazardous substances present in it, so that they cannot harm the environment, but the industries consume huge amount of water, so generation of reusable water along with the elimination of the toxic chemicals should be the ultimate goal. This makes the entire process of industrial wastewater treatment all the more complex and intriguing. For the same reason, membrane technology and AOPs are often employed as a part of post-treatment plan for biologically treated dye effluent. Membrane fouling cannot be applied to dye effluents or dyebaths directly as it will cause extensive fouling of the membranes (Van der Bruggen et al. 2001). Thus, to increase the reusability of the wastewater, often sand filtration and/or microfiltration is used as an intermediate step between biological pretreatment and nanofiltration (Marcucci et al. 2002; Rozzi et al. 1999). It has also been reported that membrane life can be enhanced by treatment of the wastewater by suitable AOPs before the application of nanofiltration technology (Bes-Pía et al. 2004; Kang et al. 2003). Membranes with suitable pore size can be used for filtration of dye effluents such that the dye molecules are retained, while salt water is allowed to pass. The dyebath water can be reused, while an anaerobic digester can be used for the subsequent degradation of the membrane concentrate (Hai et al. 2007).

- *Membrane Bioreactors.*

Membrane bioreactors (MBRs) are the combination of a membrane process (like ultrafiltration or microfiltration) with a suspended growth bioreactor and have widespread use in the industrial wastewater treatment processes. It is a significant innovation over the conventional activated sludge treatments (Visvanathan et al. 2000). The main advantages of MBR include production of high-quality discharge water, less amount of sludge, and requirement of small area for functioning as the membranes can be installed within the reactors itself. The rate of nitrogen and phosphorus removal is quite high in this type of systems. It also increases the reusability of chemicals used in the process of dyeing. Studies have been conducted with MBRs and textile wastewater as the influent where successful removal of color along with the reduction of other wastewater pollution parameters like BOD, COD, and suspended solids was achieved, thus proving to be a remarkable option for colored wastewater treatment (Friha et al. 2015). MBR has often been coupled with adsorption for enhanced decolorization of dye effluents (Hai et al. 2007). With the discovery of MBR, it has been looked upon as a wise option for a multistep treatment process focusing mainly with the production of reusable water. It can be used as the primary treatment followed by a polishing nanofiltration step (Schoeberl et al. 2004). White rot fungi are known for their excellent degradation capacity as they can produce non-specific extracellular oxidases. These have been used with MBRs and have been found to be quite a significant innovation for increased color removal (Li et al. 2005).

17.6 Role of Nanotechnology in Decolorization and Degradation of Azo Dyes (Nano-bioremediation)

A *nanoparticle* (or nanopowder or nanocluster or nanocrystal) is a microscopic particle having at least one dimension less than 100 nm. *These* are of great scientific interest as they effectively form a bridge between bulk materials and atomic or molecular structures and are being used in numerous fields of science and technology, even in environmental remediation (Gross 2001). These particles exhibit unique properties different from those of bulk matter and have shown remarkable potential in removing contaminants. Degradation of Orange G, a monoazo dye, in aqueous solutions was studied using Fe–Ni bimetallic nanoparticles (Bokare et al. 2008). Nowadays biogenic nanoparticles are being used for dye degradation in place of the metallic ones. Iron nanoparticles from extracts of green tea leaves were used for the degradation study of Methylene Blue and Methyl Orange dyes (Shahwan et al. 2011). Anacardium occidentale testa derived silver nanoparticles (AgNPs) were found to act as catalysts in the degradation of Congo Red and Methyl Orange (Edison et al. 2016).

17.7 Conclusion

Dyes make our world colorful, but at the same time, these synthetic compounds do not fail to harm our environment. Dye effluents are significant sources of water pollution when they are discharged into the water bodies. The physical methods deal with simple separation of the toxic molecules from our source of interest and have nothing to do with degradation. The chemical methods, apart from being costly, have to introduce other chemicals and reagents to bring about degradation of these compounds. These methods generate huge amount of sludge as secondary pollutant, and often the degradation is partially complete resulting in even more toxic products. Biological treatments are greatly favorable, only that these molecules recalcitrant in nature cause major problem. Residual dyes along with other reagents used for processing are impurities that impose huge load on the wastewater treatment system and eventually reduce the efficiency of the system. Though the regulations for the discharge of dye wastewater are getting stringent with the passage of time, it only helps in increasing the cost of treatment. All these concerns have led to the development of hybrid technologies which integrates individual and combined treatment techniques in sequential or simultaneous manner. The biological methods due to their intrinsic advantages cut short on the cost of treatment if they can be applied suitably in a multistep treatment plan. For proposing suitable hybrid techniques, it is necessary to have a wise knowledge about the cost involved in the processes as well as the characteristics of the effluent to be treated. The choice of techniques should be case specific. Improper selection of methods can not only render the process unsuccessful but at the same time can be immensely cost intensive. Moreover, the goal should be not only sanitization of the effluents but also regeneration of water, chemicals, and the dye auxiliaries used in the industries along with economic feasibility; it is only then the treatment plan can be acknowledged as successful.

References

Abu-Salah K, Shelef G, Levanon D, Armon R, Dosoretz CG (1996) Microbial degradation of aromatic and polyaromatic toxic compounds adsorbed on powdered activated carbon. J Biotechnol 51:265–272

Acuner E, Dilek FB (2004) Treatment of tectilon yellow 2G by *Chlorella vulgaris*. Process Biochem 39:623–631

Adedayo O, Javadpor S, Taylor C, Anderson WA, Moo-Young M (2004) Decolourization and detoxification of methyl red by aerobic bacteria from wastewater treatment plant. World J Microbiol Biotechnol 20:545–550

Ahn DH, Chang WS, Yoon TI (1999) Dyestuff wastewater treatment using chemical oxidation, physical adsorption and fixed bed biofilm process. Process Biochem 34:429–439

Akkaya G, Uzun I, Güzel F (2007) Kinetics of the adsorption of reactive dyes by chitin. Dyes Pigments 73:168–177

Aksu Z, Tezer S (2005) Biosorption of reactive dyes on the green alga *Chlorella vulgaris*. Process Biochem 40:1347–1361

Alaton IA, Balcioglu IA (2001) Advanced oxidation of raw and biotreated textile industry wastewater with O_3, H_2O_2/UV-C and their sequential application. J Chem Technol Biotechnol 76:53–60

Alaton IA, Balcioglu IA, Bahnemann DW (2002) Advanced oxidation of a reactive dyebath effluent: comparison of O_3, H_2O_2/UV-C and TiO_2/UV-A processes. Water Res 36:1143–1154

Alaton IA (2003) A review of the effects of dye-assisting chemicals on advanced oxidation of reactive dyes in wastewater. Color Technol 119:345–353

Aleboyeh A, Aleboyeh H, Moussa Y (2003) Critical effect of hydrogen peroxide in photochemical oxidative decolorization of dyes: acid orange 8, acid blue 74 and methyl orange. Dyes Pigments 57:67–75

Alkaya E, Demirer GN (2014) Sustainable textile production: a case study from a woven fabric manufacturing mill in Turkey. J Clean Prod 65:595–603

Ambrosio ST, Vilar JC, da Silva CAA, Okada K, Nascimento AE, Longo RL (2012) A biosorption isotherm model for the removal of reactive azo dyes by inactivated mycelia of *Cunninghamella elegans* UCP542. Molecules 17:452–462

Amini M, Arami M, Mahmoodi NM, Akbari A (2011) Dye removal from colored textile wastewater using acrylic grafted nanomembrane. Desalination 267:107–113

An H, Qian Y, Gu X, Tang WZ (1996) Biological treatment of dye wastewaters using an anaerobic-oxic system. Chemosphere 33:2533–2542

An TC, Zhu XH, Xiong Y (2002) Feasibility study of photoelectrochemical degradation of methylene blue with three-dimensional electrode-photocatalytic reactor. Chemosphere 46:897–903

Anjaneyulu Y, Chary NS, Raj DSS (2005) Decolourization of industrial effluents- available methods and emerging technologies. Rev Environ Sci Biotechnol 4:245–273

Asgher M, Kausar S, Bhatti HN, Shah SAH, Ali M (2008) Optimization of medium for decolorization of solar golden yellow R direct textile dye by *Schizophyllum commune* IBL-06. Int Biodeterior Biodegrad 61:189–193

Attia AA, Girgis SB, Fathy NA (2008) Removal of methylene blue by carbons derived from peach stones by H_3PO_4 activation: batch and column studies. Dyes Pigments 76:282–289

Aubert S, Schwitzguebel JP (2004) Screening of plant species for the phytotreatment of wastewater containing sulphonated anthraquinones. Water Res 38:3569–3575

Ayed L, Cheriaa J, Laadhari N, Cheref A, Bakhrouf A (2009) Biodegradation of crystal violet by an isolated *Bacillus* sp. Ann Microbiol 59:267–272

Aziz MA, Ng WJ (1993) Industrial wastewater treatment using an activated algae-reactor. Water Sci Technol 28:71–76

Babel S, Kurniwan TA (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *J Hazard Mater* 97:219–243

Balcıoğlu IA, Alaton IA, Ötker M, Bahar R, Bakar N, Ikiz M (2003) Application of advanced oxidation processes to different industrial wastewaters. J Environ Sci Health A 38:1587–1596

Banat IM, Nigam P, Singh D, Marchant R (1996) Microbial decolorization of textile-dye-containing effluents. Bioresour Technol 58:217–227

Bandara J, Morrison C, Kiwi J, Pulgarin C, Peringer P (1996) Degradation/decoloration of concentrated solutions of Orange II. Kinetics and quantum yield for sunlight induced reactions via Fenton type reagents. J Photochem Photobiol A Chem 99:57–66

Barragan BE, Costa C, Marquez MC (2007) Biodegradation of azo dyes by bacteria inoculated on solid media. Dyes Pigments 75:73–81

Batzias FA, Sidiras DK (2007) Dye adsorption by pre-hydrolysed beech sawdust in batch and fixed-bed systems. Bioresour Technol 98:1208–1217

Bayramoglu M, Eyvaz M, Kobya M (2007) Treatment of the textile wastewater by electrocoagulation: economic evaluation. Chem Eng J 128:155–161

Bes-Pía A, Mendoza-Roca JA, Alcaina-Miranda MI, Iborra-Clar A, Iborra-Clar MI (2002) Reuse of wastewater of the textile industry after its treatment with a combination of physico-chemical treatment and membrane technologies. Desalination 149:169–174

Bes-Piá A, Mendoza-Roca JA, Alcaina-Miranda MI, Iborra-Clar A, Iborra-Clar MI (2003) Combination of physico-chemical treatment and nanofiltration to reuse wastewater of a printing, dyeing and finishing textile industry. Desalination 157:73–80

Bes-Pía A, Iborra-Clar A, Mendoza-Roca JA, Iborra-Clar MI, Alcaina-Miranda MI (2004) Nanofiltration of biologically treated textile effluents using ozone as a pre-treatment. Desalination 167:387–392

Beydilli MI, Pavlostathis SG, Tincher WC (2000) Biological decolorization of the azo dye reactive red 2 under various oxidation-reduction conditions. Water Environ Res 72:698–705

Bhatia D, Sharma NR, Singh J, Kanwar RS (2017) Biological methods for textile dye removal from wastewater: a review. Crit Rev Environ Sci Technol 47:1836–1876

Bhatnagar A, Sillanpaa M (2010) Utilization of agroindustrial and municipal waste materials as potential adsorbents for water treatment: a review. Chem Eng J 157:277–296

Bhosale S, Saratale G, Govindwar S (2006) Biotransformation enzymes in *Cunninghamella blakesleeana* (NCIM-687). J Basic Microbiol 46:444–448

Bokare AD, Chikate RC, Rode CV, Paknikar KM (2008) Iron-nickel bimetallic nanoparticles for reductive degradation of azo dye Orange G in aqueous solution. Appl Catal, B 79:270–278

Burger S, Stolz A (2010) Characterisation of the flavin free oxygen tolerant azoreductase from *Xenophilus azovorans* KF46F in comparison to flavin-containing azoreductases. Appl Microbiol Biotechnol 87:2067–2076

Carias CC, Novais JM, Martins-Dias S (2007) *Phragmites australis* peroxidases role in the degradation of azo dye. Water Sci Technol 56:263–269

Carliell CM, Barclay SJ, Naidoo N, Buckley CA, Mulholland DA, Senior E (1995) Microbial decolourisation of a reactive azo dye under anaerobic conditions. Water SA 21:61–69

Cassidy MB, Lee H, Trevors JT (1996) Environmental applications of immobilized microbial cells: a review. J Ind Microbiol 16:79–101

Chakraborty S, Purkait MK, DasGupta S, De S, Basu JK (2003) Nanofiltration of textile plant effluent for color removal and reduction in COD. Sep Purif Technol 31:141–151

Chang JS, Lin YC (2000) Fed-batch bioreactor strategies for microbial decolorization of azo dye using a *Pseudomonas luteola* strain. Biotechnol Prog 16:979–785

Chang JS, Chou C, Lin YC, Lin PJ, Ho JY, Hu TL (2001) Kinetic characteristics of bacterial azo-dye decolorization by *Pseudomonas luteola*. Water Res 35:2841–2850

Chang JS, Chen BY, Lin YS (2004) Stimulation of bacterial decolorization of an azo dye by extracellular metabolites from *Escherichia coli* strain NO3. Bioresour Technol 91:243–248

Chaudhry Q, Zandstra MB, Gupta S, Joner EJ (2005) Utilizing the synergy between plants and rhizosphere organisms to enhance the breakdown of the organic pollutants in the. Environ Sci Pollut Res 12:34–48

Chen YH, Chang CY, Huang SF, Chiu CY, Ji D, Shang NC, Yu YH, Chiang PC, Ku Y, Chen JN (2002) Decomposition of 2-naphthalenesulfonate in aqueous solution by ozonation with UV radiation. Water Res 36:4144–4154

Chen KC, Wu JY, Liou DJ, Hwang SCJ (2003) Decolorization of the textile dyes by newly isolated bacterial strains. J Biotechnol 101:57–68

Chen BY, Chen WM, Wu FL, Chen PK, Yen CY (2008) Revealing azo-dye decolorization of indigenous *Aeromonas hydrophila* from fountain spring in Northeast Taiwan. J Chin Inst Chem Eng 39:495–501

Cho BP, Yang T, Blankenship LR, Moody JD, Churchwell M, Bebland FA (2003) Synthesis and characterization of N-demethylated metabolites of malachite green and leuco malachite green. Chem Res Toxicol 16:285–294

Christian V, Shrivastava R, Shukla D, Modi HA, Vyas BR (2005) Degradation of xenobiotic compounds by lignin degrading white rot fungi: enzymology and mechanisms involved. Indian J Exp Biol 43:301–312

Ciardelli G, Ranieri N (2001) The treatment and reuse of wastewater in the textile industry by means of ozonation and electroflocculation. Water Res 35:567–572

Cisneros RL, Espinoza AG, Litter MI (2002) Photodegradation of an azo dye of the textile industry. Chemosphere 48:393–399

Crini G (2006) Non-conventional low-cost adsorbents for dye removal: a review. Bioresour Technol 97:1061–1085

Cripps C, Bumpus JA, Aust SD (1990) Biodegradation of azo and heterocyclic dyes by *Phanerochaete chrysosporium*. Appl Environ Microbiol 56:1114–1118

Culp SJ, Beland FA (1996) Malachite green: a toxicological review. Int J Toxicol 15:219–238

Daeshwar NM, Ayazloo M, Khataee AR, Pourhassan M (2007) Biological decolorization of dye solution containing malachite green by microalgae *Cosmarium* sp. Bioresour Technol 98:1176–1182

Dalzell DJB, MacFarlane NAA (1999) The toxicity of iron to brown trout and effects on the gills: a comparison of two grades of iron sulphate. J Fish Biol 55:301–315

Daneshvar N, Ashassi-Sorkhabi H, Tizpar A (2003) Decolorization of orange II by electrocoagulation method. Sep Purif Technol 31:153–162

Daneshvar E, Kousha M, Sohrabi MS, Khataee A, Converti A (2012) Biosorption of three acid dyes by the brown macroalga *Stoechospermum marginatum*: isotherm, kinetic and thermodynamic studies. Chem Eng J 195–196:297–306

Das N, Charumathi D (2012) Remediation of synthetic dyes from wastewater using yeast: a review. Indian J Biotechnol 11:369–380

Dawkar VV, Jadhav UU, Jadhav SU, Govindwar SP (2008) Biodegradation of disperse textile dye brown 3REL by newly isolated *Bacillus* sp. VUS. J Appl Microbiol 105:14–24

Delée W, Neill CO, Hawkes FR, HRM P (1998) Anaerobic treatment of textile effluents. J Chem Technol Biotechnol 73:323–335

Deniz F, Karaman S (2011) Removal of an azo-metal complex textile dye from colored aqueous solutions using an agro-residue. Microchem J 99:296–302

Diaper D, Corriea VM, Judd SJ (1996) The use of membranes for the recycling of water and chemicals from dyehouse effluents: an economic assessment. J Soc Dyers Colour 112:272–281

Dŏgan M, Ozdemir Y, Alkan M (2007) Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite. Dyes Pigments 75:701–713

Donmez G, Asku Z (2002) Removal of chromium (VI) from saline wastewater by *Dunaliella* species. Process Biochem 38:751–762

dos Santos AB, Cervantes FJ, Lier JB (2007) Review paper on current technologies for decolourisation of textile wastewaters: perspectives for anaerobic biotechnology. Bioresour Technol 98:2369–2385

Duarte-Vazquez MA, Whitaker JR, Rojo-Dominguez A, Garcia-Almendarez BE, Regalado C (2003) Isolation and thermal characterization of an acidic iso-peroxidase from turnip roots. J Agric Food Chem 51:5096–5102

Dulkadiroglu H, Dogruel S, Okutman D, Kabdasli I, Sozen S, Orhon D (2002) Effect of chemical treatment on soluble residual COD in textile wastewaters. Water Sci Technol 45(12):251–259

Duran N, Esposito E (2000) Potential applications of oxidative enzymes and phenoloxidase-like compounds in wastewater and soil treatment: a review. Appl Catal, B 28:83–99

Edison TNJI, Atchudan R, Sethuraman MG, Lee YR (2016) Reductive-degradation of carcinogenic azo dyes using Anacardium occidentale testa derived silver nanoparticles. J Photochem Photobiol, B 162:604–610

El-Sheekh MM, Gharieb MM, Abou-El-Souod GW (2009) Biodegradation of dyes by some green algae and cyanobacteria. Int Biodeterior Biodegradation 63:699–704

Erden E, Kaymaz Y, Pazarlioglu NK (2011) Biosorption kinetics of a direct azo dye Sirius blue K-CFN by *Trametes versicolor*. Electron J Biotechnol 14:1–10

Espantaleon AG, Nieto JA, Fernandez M, Marsal A (2003) Use of activated clays in the removal of dyes and surfactants from tannery waste waters. Appl Clay Sci 24:105–110

Feijoo G, Vidal G, Moreira MT, Mendez R, Lema JM (1995) Degradation of high molecular weight compounds of kraft pulp mill effluents by a combined treatment with fungi and bacteria. Biotechnol Lett 17:1261–1266

Feitkenhauer H, Meyer U (2001) Integration of biotechnological wastewater treatment units in textile finishing factories: from end of the pipe solutions to combined production and wastewater treatment units. J Biotechnol 89:185–192

Ferreira BCS, Teodoro FS, Mageste AB, Gil LF, de Freitas RP, Gurgel LVA (2015) Application of a new carboxylate-functionalized sugarcane bagasse for adsorptive removal of crystal violet from aqueous solution: kinetic, equilibrium and thermodynamic studies. Ind Crop Prod 65:521–534

Ferreira-Leitao VS, de Carvalho MEA, Bon EPS (2007) Lignin peroxidase efficiency for methylene blue decoloration: comparison to reported methods. Dyes Pigments 74:230–236

Forgacs E, Cserháti F, Oros G (2004) Removal of synthetic dyes from wastewaters (a review). Environ Int 30:953–971

Fournier D, Halasz A, Thiboutot S, Ampleman G, Dominic M, Hawari J (2004) Biodegradation of Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine (HMX) by *Phanerochaete chrysosporium*. New insight into the degradation pathway. Environ Sci Technol 38:4130–4133

Friha I, Bradai M, Johnson D, Hilal N, Loukil S, Ben Amor F, Feki F, Han J, Isoda H, Sayadi S (2015) Treatment of textile wastewater by submerged membrane bioreactor: in vitro bioassays for the assessment of stress response elicited by raw and reclaimed wastewater. J Environ Manag 160:184–192

Frijters CTMJ, Vos RH, Scheffer G, Mulder R (2006) Decolorizing and detoxifying textile wastewater, containing both soluble and insoluble dyes, in a full scale combined anaerobic/aerobic system. Water Res 40:1249–1257

Fu F, Viraraghavan T (2001) Fungal decolorization of dye wastewaters: a review. Bioresour Technol 79:251–262

Fung PC, Huang Q, Tsui SM, Poon CS (1999) Treatability study of organic and colour removal in desizing/dyeing wastewater by UV/US system combined with hydrogen peroxide. Water Sci Technol 40:153–160

Fung PC, Poon CS, Chu CW, Tsui SM (2001) Degradation kinetics of reactive dye by UV/H2O2/US process under continuous mode operation. Water Sci Technol 44:67–72

Gadd GM (2001) Fungi in bioremediation published for the British mycological society. Cambridge University Press the Edinburgh Building, Cambridge

Gao B, Yue Q, Miao J (2001) Evaluation of polyaluminium ferric chloride (PAFC) as a composite coagulant for water and wastewater treatment. Water Sci Technol 47:127–132

Gemeay AH, Mansour IA, El-Sharkawy RG, Zaki AB (2003) Kinetics and mechanism of the heterogeneous catalyzed oxidative degradation of indigo carmine. J Mol Catal A Chem 193:109–120

Ghanem KM, Al-Fassi FA, Biag AK (2012) Optimization of methyl orange by mono and mixed bacterial culture techniques using statistical design. Afr J Microbiol Res 6:575–585

Ghodake GS, Telke AA, Jadhav JP, Govindwar SP (2009) Potential of Brssica juncea in order to treat textile effluent contaminated sites. Int J Phytoremediation 11:297–312

Gill PK, Arora DS, Chander M (2002) Biodecolorization of azo and triphenylmethane dyes by *Dichomitus squalens* and *Phlebia* spp. J Ind Microbiol Biotechnol 28:201–203

Gogate PR, Pandit AB (2004a) A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. Adv Environ Res 8:501–557

Gogate PR, Pandit AB (2004b) A review of imperative technologies for wastewater treatment II: hybrid methods. Adv Environ Res 8:553–597

Grau P (1991) Textile industry wastewaters treatment. Water Sci Technol 24:97–103

Gross M (2001) Travels to the nanoworld: miniature machinery in nature and technology. Plenum Trade, New York

Guivarch E, Trevin S, Lahitte C, Oturan MA (2003) Degradation of azo dyes in water by electro-Fenton process. Environ Chem Lett 1:38–44

Hai FI, Yamamoto K, Fukushi K (2007) Hybrid treatment systems for dye wastewater. Crit Rev Environ Sci Technol 37:315–377

Hammaini A, Ballester A, Blazquez MI, Gonzalez F, Munoz J (2002) Effect of the presence of lead on the biosorption of copper, cadmium and zinc by activated sludge. Hydrometallurgy 67:109–116

Han MH, Yun YS (2007) Mechanistic understanding and performance enhancement of biosorption of reactive dyestuffs by the waste biomass generated from amino acid fermentation process. Biochem Eng J 36:2–7

Han B, Kim J, Kim Y, Choi JS, Makarov IE, Ponomarev AV (2004) Electron beam treatment of textile dyeing wastewater: operation of pilot plant and industrial plant construction. In Proceedings of IWA world water congress, Marrakech 26258

Hao OJ, Kim H, Chiang PC (2000) Decolorization of wastewater. Crit Rev Environ Sci Technol 30:449–505

Hassan MM, Hawkyard CJ (2007) Decolorisation of effluent with ozone and re-use of spent dyebath. In: Christie RM (ed) Environmental aspects of textile dyeing. Woodhead, Cambridge, pp 149–190

Hatvani N, Mecs I (2001) Production of laccase and manganese peroxidase by *Lentinus edodes* on malt containing by-product of the brewing process. Process Biochem 37:491–496

Ho YS, Chiu WT, Wang CC (2005) Regression analysis for the sorption isotherms of basic dyes on sugarcane dust. Bioresour Technol 96:1285–1291

Hörsch P, Speck A, Frimmel FH (2003) Combined advanced oxidation and biodegradation of industrial effluents from the production of stilbene-based fluorescent whitening agents. Water Res 37:2748–2756

Humnabadkar RP, Saratale GD, Govindwar SP (2008) Decolorization of purple 2R by *Aspergillus ochraceus* (NCIM-1146). Asian J Microbiol Biotechnol Environ Sci 10:693–697

Hunger K (ed) (2003) Industrial dyes: chemistry, properties, applications, vol 4. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Jadhav JP, Govindwar SP (2006) Biotransformation of malachite green by *Saccharomyces cerevisiae* MTCC 463. Yeast 23:315–323

Jadhav JP, Parshetti GK, Kalme SD, Govindwar SP (2007) Decolorization of azo dye methyl red by *Saccharomyces cerevisiae* MTCC 463. Chemosphere 68:394–400

Jadhav UU, Dawkar VV, Ghodake GS, Govindwar SP (2008) Biodegradation of direct red 5B, a textile dye by newly isolated *Comamonas* sp. UVS. J Hazard Mater 158:507–516

Jochimsen JC, Martin R, Jekel MR (1997) Partial oxidation effects during the combined oxidative and biological treatment of separated streams of tannery wastewater. Water Sci Technol 35:337–345

Joshi M, Purwar R (2004) Developments in new processes for colour removal from effluent. Rev Prog Color 34:58–71

Joshi M, Bansal R, Purwar R (2004) Colour removal from textile effluents. Indian J Fibre Text Res 29:239–259

Joshi T, Iyengar L, Singh K, Garg S (2008) Isolation, identification and application of novel bacterial consortium TJ-1 for the decolourization of structurally different azo dyes. Bioresour Technol 99:7115–7121

Kadirvelu K, Kavipriya M, Karthika C, Radhika M, Vennilamani N, Pattabhi S (2003) Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. Bioresour Technol 87:129–132

Kagalkar AN, Jagtap UB, Jadhav JP, Bapat VA, Govindwar SP (2009) Biotechnological strategies for phytoremediation of the Sulfonated Azo dye direct red 5B using *Blumea malcolmii* hook. Bioresour Technol 100:4104–4110

Kalaiarasi K, Lavanya A, Amsamani S, Bagyalakshmi G (2012) Decolorization of textile dye effluent by non-viable biomass of *Aspergillus fumigatus*. Braz Arch Biol Technol 55:471–476

Kalme SD, Parshetti GK, Jadhav SU, Govindwar SP (2007) Biodegradation of benzidine based dye direct Blue-6 by Pseudomonas desmolyticum NCIM 2112. Bioresour Technol 98:1405–1410

Kalyani DC, Telke AA, Dhanve RS, Jadhav JP (2009) Ecofriendly biodegradation and detoxification of reactive red 2 textile dye by newly isolated *Pseudomonas* sp. SUK1. J Hazard Mater 163:735–742

Kalyuzhnyi S, Sklyar V (2000) Biomineralisation of azo dyes and their breakdown products in anaerobic-aerobic hybrid and UASB reactors. Water Sci Technol 41:23–30

Kang SF, Yen HY, Yang MH (2003) Treatment of textile effluents by H_2O_2 / UV oxidation combined with RO separation for reuse. J Environ Sci Health A 38:1327–1339

Kannan N, Murugavel S, Xavier A (2006) Photocatalytic degradation of acid orange and Congo red dyes using titanium dioxide. Indian. J Environ Prot 26:1093–1100

Kapdan IK, Kargi F (2002) Simultaneous biodegradation and adsorption of textile dyestuff in an activated sludge unit. Process Biochem 37:973–981

Khataee AR, Vafaei F, Jannatkhah M (2013) Biosorption of three textile dyes from contaminated water by filamentous green algae *Spirogyra* sp: kinetic, isotherm and thermodynamic studies. Int Biodeterior Biodegrad 83:33–40

Khehra MS, Saini HS, Sharma DK, Chadha BS, Chimni SS (2005) Decolorization of various azo dyes by bacterial consortium. Dyes Pigments 67:55–61

Khlifi R, Belbahri L, Woodward S, Ellouz M, Dhouib A, Sayadi S (2010) Decolorization and detoxification of textile industry wastewater by the laccase-mediator system. J Hazard Mater 175:802–808

Kim TH, Park C, Lee J, Shin EB, Kim S (2002) Pilot scale treatment of textile wastewater by combined process (fluidized biofilm process–chemical coagulation–electrochemical oxidation). Water Res 36:3979–3988

Kim K, Fujita M, Daimon H, Fujie K (2004a) Biodegradability improvement and structural conversion of polyvinyl alcohol by sub and supercritical water reaction. J Chem Eng Jpn 37:744–750

Kim TH, Lee Y, Yang J, Lee B, Park C, Kim S (2004b) Decolorization of dye solutions by a membrane bioreactor (MBR) using white-rot fungi. Desalination 168:287–293

Kim TH, Park C, Yang J, Kim S (2004c) Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation. J Hazard Mater 112:95–103

Kim SY, An JY, Kim BW (2008) The effects of reductant and carbon source on the microbial decolorization of azo dyes in an anaerobic sludge process. Dyes Pigments 76:256–263

Knudsen L, Pedersen JA, Munck J (1994) Advanced treatment of paper mill effluents by a two-stage activated sludge process. Water Sci Technol 30:173–181

Konstantinou IK, Albanis TA (2004) TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations. Appl Catal, B 49:1–14

Koseoglu-Imer YD (2013) The determination of performances of polysulfone (PS) ultrafiltration membranes fabricated at different evaporation temperatures for the pretreatment of textile wastewater. Desalination 316:110–119

Krapfenbauer KF, Robinson MR, Getoff N (1999) Development of and testing of TiO_2- catalysts for EDTA-radiolysis using γ-rays (1st part). J Adv Oxid Technol 4:213–217

Kraume M (2002) Transport processes and apparative applications in process technic. Springer, Heidelberg. (In German)

Kudlich M, Bishop PL, Knackmuss HJ, Stolz A (1996) Simultaneous anaerobic and aerobic degradation of the sulfonated azo dye mordant yellow 3 by immobilized cells from a naphthalenesulfonate-degradaing mixed culture. Appl Microbiol Biotechnol 46:597–603

Kumar U (2006) Agricultural products and by-products as a low cost adsorbent for heavy metal removal from water and wastewater. Sci Res Essay 1:33–37

Kumar MNVR, Sridhari TR, Bhavani KD, Dutta PK (1998) Trends in color removal from textile mill effluents. Colorage 40:25–34

Lade HS, Waghmode TR, Kadam AA, Govindwar SP (2012) Enhanced biodegradation and detoxification of disperse azo dye Rubine GFL and textile industry effluent by defined fungal-bacterial consortium. Int Biodeterior Biodegrad 72:94–107

Li CW, Lin JL, Kang SF, Liang CL (2005) Acidification and alkalization of textile chemical sludge: volume/solid reduction, de-waterability, and Al(III) recovery. Sep Purif Technol 42:31–37

Lin SH, Lin CM (1993) Treatment of textile waste effluents by ozonation and chemical coagulation. Water Res 27:1743–1748

Lin SH, Lo CC (1997) Fenton process for treatment of desizing wastewater. Water Res 31:2050–2056

Lin SH, Peng CF (1996) Continuous treatment of textile wastewater by combined coagulation, electrochemical oxidation and activated sludge. Water Res 30:587–592

Lisi RD, Lazzara G, Milioto S, Muratore N (2007) Adsorption of a dye on clay and sand. Use of cyclodextrins as solubility-enhancement agents. Chemosphere 69:11–20

Lopez A, Ricco G, Ciannarella R, Rozzi A, Pinto ACD, Passino R (1999) Textile wastewater reuse: ozonation of membrane concentrated secondary effluent. Water Sci Technol 40:99–106

Lorimer JP, Mason TJ, Plattes M, Phull SS (2000) Dye effluent decolourisation using ultrasonically assisted electro-oxidation. Ultrason Sonochem 7:237–242

Lourenço ND, Novais JM, Pinheiro HM (2001) Effect of some operational parameters on textile dye biodegradation in a sequential batch reactor. J Biotechnol 89:163–174

Lu L, Zhao M, Liang SC, Zhao LY, Li DB, Zhang BB (2009) Production and synthetic dyes decolorization capacity of a recombinant laccase from Pichia pastoris. J Appl Microbiol 107:1149–1156

Lucas MS, Amaral C, Sampaio A, Peres JA, Dias AA (2006) Diazo dye reactive black 5 by a wild isolate of *Candida oleophila*. Enzym Microb Technol 39:51–55

Machado KMG, Compart LCA, Morais RO, Rosa LH, Santos MH (2006) Biodegradation of reactive textile dyes by Basidiomycetous Fungi from Brazilian ecosystems. Braz J Microbiol 37:481–487

Malik PK (2003) Use of activated carbons prepared from sawdust and rice husk for adsorption of acid dyes: a case study of acid yellow 36. Dyes Pigments 56:239–249

Malik R, Ramteke DS, Wate SR (2007) Adsorption of malachite green on groundnut shell waste based powdered activated carbon. Waste Manag 27:1129–1138

Mantzavinos D, Psillakis E (2004) Enhancement of biodegradability of industrial wastewaters by chemical oxidation pre-treatment. J Chem Technol Biotechnol 79:431–454

Marcucci M, Ciardelli G, Matteucci A, Ranieri L, Russo M (2002) Experimental campaigns on textile wastewater for reuse by means of different membrane processes. Desalination 149:137–143

Marmagne O, Coste C (1996) Color removal from textile plant effluents. Am Dyestuff Rep 85:15–21

Márquez MC, Costa C (1997) Biomass concentration in PACT process. Water Res 30:2079–2085

Martorell MM, Pajot HF, de Figueroa LIC (2012) Dye decolorizing yeasts isolated from Las Yungas rainforest: dye assimilation and removal used as selection criteria. Int Biodeterior Biodegrad 66:25–32

Mbuligwe SE (2005) Comparative treatment of dye-rich wastewater in engineered wetland systems (EWSs) vegetated with different plants. Water Res 39:271–280

McMullan G, Meehan C, Conneely A, Kirby N, Robinson T, Nigam P, Banat IM, Smyth WF (2001) Microbial decolorization and degradation of textile dyes. Appl Microbiol Biotechnol 56:81–87

Mendes S, Pereira L, Batista C, Martins LO (2011) Molecular determinants of azo reduction activity in the strain *Pseudomonas putida* MET94. Appl Microbiol Biotechnol 92:393–405

Méndez-Paz D, Omil F, Lema JM (2005) Anaerobic treatment of azo dye acid orange 7 under batch conditions. Enzym Microb Technol 36:264–272

Meyers RA (1998) Encyclopedia of environmental analysis and remediation. Wiley, New York, pp 1422–1465

Misal SA, Lingojwar DP, Shinde RM, Gawai KR (2011) Purification and characterization of azoreductase from alkaliphilic strain *Bacillus badius*. Process Biochem 46:1264–1269

Miyata N, Mori T, Iwahori K, Fujita M (2000) Microbial decolorization of melanoidin-containing wastewaters: combined use of activated sludge and the fungus *Coriolus hirsutus*. J Biosci Bioeng 89:145–150

Mohan SV, Rao CN, Prasad KK, Karthikeyan J (2002) Treatment of simulated reactive yellow 22 (azo) dye effluents using *Spirogyra* species. Waste Manag 22:575–582

Molinari R, Pirillo F, Falco M, Loddo V, Palmisano L (2004) Photocatalytic degradation of dyes by using a membrane reactor. Chem Eng Process 43:1103–1114

Moraes SG, Freire RS, Durán N (2002) Degradation and toxicity reduction of textile effluent by combined photocatalytic and ozonation processes. Chemosphere 40:369–373

Mrowetz M, Pirola C, Selli E (2003) Degradation of organic water pollutants through sonophotocatalysis in the presence of TiO_2. Ultrason Sonochem 10:247–254

Muruganandham M, Swaminathan M (2004) Photochemical oxidation of reactive azo dye with UV–H_2O_2 process. Dyes Pigments 62:269–275

Naim MM, El Abd YM (2002) Removal and recovery of dyestuffs from dyeing wastewaters. Sep Purif Methods 31:171–228

Namboodri CG, Perkins WS, Walsh WK (1994a) Decolorizing dyes with chlorine and ozone, Part I Amer. Dyestuff Rep 83:17–22

Namboodri CG, Perkins WS, Walsh WK (1994b) Decolorizing dyes with chlorine and ozone, Part II Amer. Dyestuff Rep 83:17–25

Nascimento C, Magalhães DP, Brandão M, Santos AB, Chame M, Baptista D, Nishikawa M, da Silva M (2011) Degradation and detoxification of three textile azo dyes by mixed fungal cultures from semi-arid region of Brazilian Northeast. Braz Arch Biol Technol 54:621–628

Neamtu M, Siminiceanu I, Yediler A, Kettrup A (2002) Kinetics of decolorization and mineralization of reactive azo dyes in aqueous solution by the UV/H_2O_2 oxidation. Dyes Pigments 53:93–99

Nicolet L, Rott U (1999) Recirculation of powdered activated carbon for the adsorption of dyes in municipal wastewater treatment plants. Water Sci Technol 40:191–198

Nigam P, Banat IM, Singh D, Marchant R (1996) Microbial process for the decolorization of textile effluents containing azo, diazo and reactive dyes. Process Biochem 31:435–442

O'Neill C, Lopez A, Esteves S, Hawkes FR, Wilcox S (2000) Azo-dye degradation in an anaerobic-aerobic treatment system operating on simulated textile effluent. Appl Microbiol Biotechnol 53:249–254

Ong ST, Lee CK, Zainal Z (2007) Removal of basic and reactive dyes using ethylenediamine modified rice hull. Bioresour Technol 98:2792–2799

Ozacar M, Sengil AI (2005) Adsorption of metal complex dyes from aqueous solutions by pine sawdust. Bioresour Technol 96:791–795

Pajot HF, de Figueroa LIC, JI F˜n (2007) Dye-decolorizing activity in isolated yeasts from the ecoregion of Las Yungas (Tucuman, Argentina). Enzym Microb Technol 40:1503–1511

Pajot HF, Delgado O, de Figueroa LIC, Farina JI (2011) Unraveling the decolorizing ability of yeast isolates from dye polluted and virgin environment: An ecological and taxonomical overview. Antonie Van Leeuwenhoek 99:443–456

Pandey A, Singh P, Iyengar L (2007) Bacterial decolorization and degradation of azo dyes (a review). Int Biodeterior Biodegrad 59:73–84

Panswad T, Techovanich A, Anotai J (2001) Comparison of dye wastewater treatment by normal and anoxic+anaerobic/aerobic SBR activated sludge processes. Water Sci Technol 43:355–362

Papic S, Koprivanac N, Bozic AL, Metes A (2004) Removal of some reactive dyes from synthetic wastewater by combined Al (III) coagulation/carbon adsorption process. Dyes Pigments 62:291–298

Parikh A, Madamwar D (2005) Textile dye Decolorization using cyanobacteria. Biotechnol Lett 27:323–326

Patil P, Desai N, Govindwar S, Jadhav JP, Bapat V (2009) Degradation analysis of reactive red 198 by hairy roots of *Tagetes Patula* L. (Marigold). Planta 230:725–735

Perkowski J, Kos L (2003) Decolouration of model dyehouse wastewater with advanced oxidation processes. Fibres Text East Eur 11:67–71

Phugare S, Patil P, Govindwar S, Jadhav J (2010) Exploitation of yeast biomass generated as a waste product of distillery industry for remediation of textile industry effluent. Int Biodeterior Biodegrad 64:716–726

Pintar A, Besson M, Gallezot P, Gibert J, Martin D (2004) Toxicity to *Daphnia magna* and *Vibrio fischeri* of Kraft bleach plant effluents treated by catalytic wet-air oxidation. Water Res 38:289–300

Qing T, Chen J, Xi D, Hua Z (2004) Study on the enriched oxygen BAC method in the advanced treatment of textile dying-printing and alkali peeling wastewater. In Proceedings of IWA world water congress, Marrakech 28287

Rabaey K, Van de Sompel K, Maignien L, Boon N, Aelterman P, Clauwaert P, De Schamphelaire L, Pham HT, Vermeulen J, Verhaege M, Lens P, Verstraete W (2006) Microbial fuel cells for sulfide removal. Environ Sci Technol 40:5218–5224

Rahman IR, Saad B, Shaidan S, Sya RES (2005) Adsorption characteristics of malachite green on activated carbon derived from rice husks produced by chemical-thermal process. Bioresour Technol 96:1578–1583

Rai HS, Bhattacharya MS, Singh J, Bansal TK, Vats P, Banerjee UC (2005) Removal of dyes from the effluent of textile and dyestuff manufacturing industry: a review of emerging techniques with reference to biological treatment. Crit Rev Environ Sci Technol 35:219–238

Rajaguru P, Kalaiselvi K, Palanivel M, Subburam V (2000) Biodegradation of azo dyes of azo dyes in a sequential anaerobic-aerobic system. Appl Microbiol Biotechnol 54:268–273

Ramakrishna KR, Viraraghavan T (1997) Use of slag for dye removal. Waste Manag 17:483–488

Ramalho PA, Cardoso MH, Cavaco-Paulo A, An Ramalho MT (2004) Characterization of azo reduction activity in a novel ascomycete yeast strain. Appl Environ Microbiol 70:2279–2288

Ranade V, Bhandari V (2014) Industrial wastewater treatment, recycling and reuse, 1st edn. Elsevier Science and Technology, Oxford, Butterworth-Heinemann

Randall S, Harper D, Brierley B (1999) Ecological and ecophysiological impacts of ferric dosing in reservoirs. Hydrobiologia 395(/396):355–364

Rauf MA, Shehadi IA, Hassan WW (2007) Studies on the removal of neutral red on sand from aqueous solution and its kinetic behaviour. Dyes Pigments 75:723–726

Rawat D, Mishra V, Sharma RS (2016) Detoxification of azo dyes in the context of environmental processes. Chemosphere 155:591–605

Reddy RD, Dinesh KG, Anandan S, Sivasankar T (2016) Sonophotocatalytic treatment of Naphthol blue black dye and real textile wastewater using synthesized Fe doped TiO. Chem Eng Process 99:10–18

Renganathan S, Thilagaraj WR, Miranda LR, Gautam P, Velan M (2006) Accumulation of acid orange 7, acid red 18 and reactive black 5 by growing *Schizophyllum commune*. Bioresour Technol 97:2189–2193

Reyes J, Dezotti M, Manslla H, Villasenor J, Esposito E, Duran N (1998) Biomass photochemistry-XXII: combined photochemical and biological process for treatment of Kraft E1 effluent. Appl Catal, B 15:211–219

Robinson T, McMullan G, Marchant R, Nigam P (2001) Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresour Technol 77:247–255

Robinson T, Chandran B, Nigam P (2002) Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. Water Res 36:2824–2830

Rozzi A, Malpei F, Bonomo L, Bianchi R (1999) Textile wastewater reuse in northern Italy (COMO). Water Sci Technol 39:121–128

Saini RD (2017) Textile organic dyes: polluting effects and elimination methods from textile waste water. Int J Chem Eng Res 9:121–136

Salokhe MD, Govindwar SP (2003) Effect of carbon source on the biotransformation enzymes in *Serratia marcescens*. World J Microbiol Biotechnol 19:199–200

Saratale GD, Kalme SD, Govindwar SP (2006) Decolorization of textile dyes by *Aspergillus ochraceus*. Indian J Biotechnol 5:407–410

Saratale GD, Bhosale SK, Kalme SD, Govindwar SP (2007a) Biodegradation of kerosene in *Aspergillus ochraceus* (NCIM 1146). J Basic Microbiol 47:400–405

Saratale GD, Humnabadkar RP, Govindwar SP (2007b) Study of mixed function oxidase system in *Aspergillus ochraceus* (NCIM 1146). Indian J Microbiol 47:304–309

Saratale RG, Saratale GD, Chang JS, Govindwar SP (2009a) Decolorization and biodegradation of textile dye navy blue HER by *Trichosporon beigelii* NCIM-3326. J Hazard Mater 166:1421–1428

Saratale RG, Saratale GD, Kalyani DC, Chang JS, Govindwar SP (2009b) Enhanced decolorization and biodegradation of textile azo dye Scarlet R by using developed microbial consortium-GR. Bioresour Technol 100:2493–2500

Saratale RG, Saratale GD, Chang JS, Govindwar SP (2009c) Ecofriendly Decolorization and degradation of reactive green 19A using *Micrococcus glutamicus* NCIM-2168. Bioresour Technol 110:3897–3905

Saratale RG, Saratale GD, Chang JS, Govindwar SP (2011) Bacterial decolorization and degradation of azo dyes: a review. J Taiwan Inst Chem Eng 42:138–157

Satiroglu N, Yalcinkaya Y, Denizli A, Arica MY, Bektas S, Genc O (2002) Application of NaOH treated *Polyporus versicolor* for removal of divalent ions of group IIB elements from synthetic wastewater. Process Biochem 38:65–72

Savin II, Butnaru R (2008) Wastewater characteristics in textile finishing mills. Environ Eng Manag J 7:859–864

Schoeberl P, Brik M, Braun R, Fuchs W (2004) Treatment and recycling of textile wastewater-case study and development of a recycling concept. Desalination 171:173–183

Senan RC, Abraham TE (2004) Bioremediation of textile azo dyes by aerobic bacterial consortium. Biodegradation 15:275–280

Shah MP (2018) Azo dye removal technologies. Austin J Biotechnol Bioeng 5:1090–1096

Shah V, Verma P, Stopka P, Gabriel J, Baldrian P, Nerud F (2003) Decolorization of dyes with copper (II)/organic acid/hydrogen peroxide systems. Appl Catal, B 46:287–292

Shahwan T, Sirriah SA, Nairat M, Boyaci E, Eroglu AE, Scott TB, Hallam KR (2011) Green synthesis of iron nanoparticle and their application as a Fenton-like catalyst for the degradation of aqueous cationic and anionic dyes. Chem Eng J 172:258–266

Shende RV, Mahajani VV (2002) Wet oxidative regeneration of activated carbon loaded with reactive dye. Waste Manag 22:73–83

Sheth N, Dave S (2010) Enhanced biodegradation of reactive violet 5R manufacturing wastewater using down flow fixed film bioreactor. Bioresour Technol 101:8627–8631

Shinde UG, Metkar SK, Bodkhe RL, Khosare GY, Harke SN (2012) Potential of polyphenol oxidases of *Parthenium hysterophorus*, *Alternanthera sessilis* and *Jotrapha curcas* for simultaneous degradation of two textiles dyes: yellow 5G and Brown R. Trends Biotechnol Res 1:24–28

Singh K, Arora S (2011) Removal of synthetic textile dyes from wastewaters: a critical review on present treatment technologies. Crit Rev Environ Sci Technol 41:807–878

Singh PK, Singh RL (2017) Bio-removal of Azo dyes: a review. Int J Appl Sci Biotechnol 5:108–126

Solpan D, Güven O, Takács E, Wojnárovits L, Dajka K (2003) High-energy irradiation treatment of aqueous solutions of azo dyes: steady-state gamma radiolysis experiments. Radiat Phys Chem 67:531–534

Specchia V, Gianetto A (1984) Powdered activated carbon in an activated sludge treatment plant. Water Res 18:133–137

Sponza DT, Işik M (2002) Decolorization and azo dye degradation by anaerobic/aerobic sequential process. Enzym Microb Technol 31:102–110

Srinivasan A, Viraraghavan T (2010) Decolorization of dye wastewaters by biosorbents: a review. J Environ Manag 91:1915–1929

Stolz A (2001) Basic and applied aspects in the microbial degradation of azo dyes. Appl Microbiol Biotechnol 56:69–80

Subramaniam R, Ponnusamy SK (2015) Novel adsorbent from agricultural waste (cashew NUT shell) for methylene blue dye removal: optimization by response surface methodology. Water Resour Ind 11:64–75

Sugiarto AT, Ohshima T, Sato M (2002) Advanced oxidation processes using pulsed streamer corona discharge in water. Thin Solid Films 407:174–178

Sun J, Hu YY, Bi Z, Cao YQ (2009) Simultaneous decolorization of azo dye and bioelectricity generation using a microfiltration membrane air-cathode single chamber microbial fuel cell. Bioresour Technol 100:3185–3192

Swaminathan K, Sandhya S, Sophia AS, Pachhade K, Subrahmanyam YV (2003) Decolorization and degradation of H-acid and other dyes using ferrous-hydrogen peroxide system. Chemosphere 50:619–625

Tay JH, Chen D, Sun DD (2001) Removal of color substances using photocatalytic oxidation for membrane filtration processess. Water Sci Technol 43:319–325

Telke A, Kalyani D, Jadhav J, Kinetics GS (2008) Mechanism of reactive red 141 degradation by a bacterial isolate *Rhizobium* radiobacter MTCC 8161. Acta Chim Slov 55:320–329

Telke AA, Ghodake GS, Kalyani DC, Dhanve RS, Govindwar SP (2011) Biochemical characteristics of a textile dye degrading extracellular laccase from a *Bacillus* sp. ADR. Bioresour Technol 102:1752–1756

Torrades F, García-Montaño J, García-Hortal JA, Domènech X, Peral J (2004) Decolorization and mineralization of commercial reactive dyes under solar light assisted photo-Fenton conditions. Sol Energy 77:573–581

Torres E, Bustos-Jaimes I, Le Borgne S (2003) Potential use of oxidative enzymes for the detoxification of organic pollutants. Appl Catal, B 46:1–15

Tunc O, Tanacı H, Aksu Z (2009) Potential use of cotton plant wastes for the removal of Remazol black B reactive dye. J Hazard Mater 163:187–198

Uygur A (1997) An overview of oxidative and photooxidative decolorisation treatments of textile wastewaters. J Soc Dye Colour 113:211–217

Van Anholt RD, Spanings FAT, Knol AH, Velden JA, Wendelaar Bonga SE (2002) Effects of iron sulfate dosage on the water flea (*Daphnia magna Straus*) and early development of carp (*Cyprinus carpio* L.). Arch Environ Contam Toxicol 42:182–192

Van der Bruggen B, De Vreese I, Vandecasteele C (2001) Water reclamation in the textile industry: nanofiltration of dye baths for wool dyeing. Ind Eng Chem Res 40:3973–3978

Vidal G, Nieto J, Mansilla HD, Bornhardt C (2004) Combined oxidative and biological treatment of separated streams of tannery wastewater. Water Sci Technol 49:287–292

Vijayaraghavan K, Yun YS (2007) Utilization of Fermentation Waste (*Corynebacterium glutamicum*) for Biosorption of Reactive Black 5 from Aqueous Solution. J Hazard Mater 141:45–52

Visvanathan C, Ben Aim R, Parameshwaran R (2000) Membrane separation bioreactors for wastewater treatment. Crit Rev Env Sci Technol 30:1–48

Vitor V, Corso CR (2008) Decolorization of textile dye by isolated *Candida albicans* from industrial effluents. J Ind Microbiol Biotechnol 35:1353–1357

Walker GM, Weatherley LR (1997) A simplified predictive model for biologically activated carbon fixed beds. Process Biochem 32:327–335

Weixing S, Xiangjing X, Gang S (1998) Chemically modified sunflower stalks as adsorbents for color removal from textile wastewater. J Appl Polym Sci 71:1841–1850

Willmott N, Guthrie J, Nelson G (1998) The biotechnology approach to colour removal from textile effluent. J Soc Dye Colour 114:38–41

Wu WT, Jean MD (2012) Evaluation of light irradiation on decolorization of azo dyes by *Tsukamurella* sp. J8025. Appl Mech Mater 145:304–308

Wu R, Qu J, He H, Yu Y (2004) Removal of azo-dye acid red B (ARB) by adsorption and catalytic combustion using magnetic $CuFe_2O_4$ powder. Appl Catal, B 48:49–56

Wuhrmann K, Mechsner K, Kappeler T (1980) Investigations on rate determining factors in the microbial reduction of azo dyes. Eur J Appl Microbiol Biotechnol 9:325–338

Xiaojian Z, Zhansheng W, Xiasheng G (1991) Simple combination of biodegradation and carbon adsorption- the mechanism of the biological activated carbon process. Water Res 25:165–172

Xu XR, Li HB, Wang WH, Gu JD (2004) Degradation of dyes in aqueous solutions by the Fenton process. Chemosphere 57:595–600

Xu XR, Li HB, Wang WH, Gu JD (2005) Decolorization of dyes and textile wastewater by potassium permanganate. Chemosphere 59:893–898

Yang Y, Wyatt IIDT, Bahorsky M (1998) Decolorisation of dyes using UV/H_2O_2 photochemical oxidation. Text Chem Color 30:27–35

Yang Q, Yang M, Pritsch K, Yediler A, Hagn A, Schloter M, Kettrup A (2003) Decolorization of synthetic dyes and production of manganese-dependent peroxidase by new fungal isolates. Biotechnol Lett 25:709–713

Yu Z, Wen X (2005) Screening and identification of yeasts for decoloring synthetic dyes in industrial wastewater. Int Biodeterior Biodegrad 56:109–114

Yung-Kyu P, Chul-Hee L (1996) Dyeing wastewater treatment by activated sludge process with a polyurethane fluidized bed biofilm. Water Sci Technol 34:193–200

Yurtsever A, Sahinkaya E, Aktas Ö, Uçar D, Çınar Ö, Wang Z (2015) Performances of anaerobic and aerobic membrane treatment of synthetic textile wastewater. Bioresour Technol 192:564–573

Zaoyan Y, Ke S, Guangliang S, Fan Y, Jinshan D, Huanian M (1992) Anaeroicaerobic treatment of a dye wastewater by combination of RBC with activated sludge. Water Sci Technol 26:2093–2096

Zee FP, Bisschops IAE, Lettinga G, Field JA (2003) Activated carbon as an electron acceptor and redox mediator during the anaerobic biotransformation of Azo dyes. Environ Sci Technol 37:402–408

Zhang X, Flurkey W (1997) Phenoloxidases in portabella mushrooms. J Food Sci 62:97–100

Zhang F, Yu J (2000) Decolourisation of acid violet 7 with complex pellets of white rot fungus and activated carbon. Bioprocess Eng 23:295–301

Zhang W, An T, Xiao X, Fu J, Sheng G, Cui M, Li G (2003) Photoelectrocatalytic degradation of reactive brilliant orange K-R in a new continuous flow photoelectrocatalytic reactor. Appl Catal, A 255:221–229

Zhu MX, Lee L, Wang HH, Wang Z (2007) Removal of an anionic dye by adsorption/precipitation processes using alkaline white mud. J Hazard Mater 149:735–741