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Mu. Naushad
Eric Lichtfouse *Editors*

Green Materials for Wastewater Treatment

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Mu. Naushad • Eric Lichtfouse
Editors

Green Materials for Wastewater Treatment

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Editors
Mu. Naushad
Department of Chemistry, College of Science
King Saud University
Riyadh, Saudi Arabia

Eric Lichtfouse
Aix Marseille University, CNRS, IRD
INRA, Coll France, CEREGE
Aix-en-Provence, France

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Preface

Wastewater contains various types of pollutants that have to be removed before the water is directed to surface water or groundwater. This book focuses on wastewater treatment using green and eco-friendly materials. Sustainable solutions for wastewater treatment are addressed. This book presents an overview on environmental issues associated with direct and indirect wastewater uses and various types of pollutants present in water and their health effects. The applications of various types of green materials from agricultural waste and activated carbon, and magnetic materials for wastewater treatment are discussed. This book also includes detailed reviews on the removal of phenols and pesticides; and on the use of ionic liquid modified activated carbon for the treatment of textile wastewater. Since the book presents the fundamental techniques for wastewater treatment, it will bring great benefits to readers as they would gain better understanding about the green materials and their applications for wastewater treatment. We believe this book will be useful for environmental scientists, analytical chemist, chemical engineers, materials scientists, and all researchers who are working in the field of wastewater treatment.

Riyadh, Saudi Arabia — Mu. Naushad
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> Coming together is a beginning; Keeping together is progress; Working together is success.
> (By Henry Ford)

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Mu. Naushad
Eric Lichtfouse

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About the Editors

Mu. Naushad is presently working as an Associate Professor in the Department of Chemistry, College of Science, King Saud University (KSU), Riyadh, Kingdom of Saudi Arabia. He obtained his MSc and PhD degree in Analytical Chemistry from Aligarh Muslim University, Aligarh, India, in 2002 and 2007, respectively. He has a vast research experience in the fields of analytical chemistry, materials chemistry, and environmental science. He holds several US patents, over 290 publications in the international journals of repute, 20 book chapters, and several books published by renowned international publishers. He has >7500 citations with a Google Scholar h-index of >52. He has successfully run several research projects funded by the National Plan for Science, Technology and Innovation (NPST) and King Abdulaziz City for Science and Technology (KACST), Kingdom of Saudi Arabia. He is the Editor/Editorial Member of several reputed journals like *Scientific Reports* (Nature), *Process Safety and Environmental Protection* (Elsevier), *Journal of Water Process Engineering* (Elsevier), and *International Journal of Environmental Research and Public Health* (MDPI). He is also the Associate Editor for *Environmental Chemistry Letters* (Springer) and *Desalination and Water Treatment* (Taylor & Francis). He has been awarded the Scientist of the Year Award (2015) from the National Environmental Science Academy, Delhi, India, Scientific Research Quality award (2019) from King Saud University and Almarai Award (2017), Saudi Arabia.

Eric Lichtfouse (PhD), born in 1960, is an Environmental Chemist working at the University of Aix-Marseille, France. He has invented carbon-13 dating, a method that allows the measurement of the relative age and turnover of molecular organic compounds occurring in different temporal pools of any complex media. He is teaching scientific writing and communication and has published the book *Scientific Writing for Impact Factor Journals*, which includes a new tool—the Micro-Article—to identify the novelty of research results. He is Founder and Chief Editor of scientific journals and series in environmental chemistry and agriculture. He got the Analytical Chemistry Prize by the French Chemical Society, the Grand Prize of the Universities of Nancy and Metz, and a Journal Citation Award by the Essential Indicators.

Contributors

Anandraj Akash Faculty of Natural Sciences and Faculty of Engineering, Mangosuthu University of Technology, Durban, South Africa

Tanvir Arfin Environmental Materials Division, CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), Nagpur, India

Claudia Letizia Bianchi Università degli Studi di Milano, Dip. Chimica and INSTM-UdR Milano, Milan, Italy

Dumitru Bulgariu Faculty of Geography and Geology, "Al. I. Cuza" University of Iasi, Iaşi, Romania
Romanian Academy, Filial of Iasi, Collective of Geography, Iaşi, Romania

Laura Bulgariu Faculty of Chemical Engineering and Environmental Protection Cristofor Simionescu, Department of Environmental Engineering and Management, Technical University Gheorghe Asachi of Iaşi, Iaşi, Romania

Joseph K. Bwapwa School of Engineering, Howard College, University of Kwazulu-Natal, Durban, South Africa
Faculty of Natural Sciences and Faculty of Engineering, Mangosuthu University of Technology, Durban, South Africa

Giuseppina Cerrato Università degli Studi di Torino, Dipartimento di Chimica and NIS Interdepartmental Centre and Consorzio INSTM-UdR, Torino, Italy

Saif Ali Chaudhry Environmental Chemistry Research Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi, India

Meenakshi Choudhary Swiss Institute for Dryland Environmental and Energy Research, Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Beersheba, Israel

Nirajan Dhakal Environmental Engineering and Water Technology Department, IHE Delft Institute for Water Education, Delft, The Netherlands

Ridha Djellabi Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, People's Republic of China
Department of Environmental Engineering, College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen, People's Republic of China
Laboratory of Water Treatment and Valorization of Industrial Wastes, Chemistry Department, Faculty of Sciences, Badji-Mokhtar University, Annaba, Algeria

Raj Kumar Dutta Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee, India
Centre of Nanotechnology, Indian Institute of Technology Roorkee, Roorkee, India

Mohamed Fouzi Ghorab Laboratory of Water Treatment and Valorization of Industrial Wastes, Chemistry Department, Faculty of Sciences, Badji-Mokhtar University, Annaba, Algeria

Penny P. Govender Department of Applied Chemistry, Doornfontein Campus 2028, University of Johannesburg, Johannesburg, South Africa

Girish M. Joshi Department of Engineering Physics and Engineering Materials, Institute of Chemical Technology (ICT), Jalna, Maharashtra, India

Jaskiran Kaur Department of Environmental Science and Technology, School of Environment and Earth Sciences, Central University of Punjab, Bathinda, India

Rizwan Khan Department of Chemistry, Chaudhary Charan Singh University, Meerut, Uttar Pradesh, India

Samreen Heena Khan School of Nano Sciences, Central University of Gujarat, Gandhinagar, India

Ilango Aswin Kumar Department of Chemistry, Anna University, University College of Engineering – Dindigul, Dindigul, Tamil Nadu, India

P. Senthil Kumar Department of Chemical Engineering, SSN College of Engineering, Chennai, India

S. Muthusaravanan Laboratory for Bioremediation Research, Unit Operations Laboratory, Department of Biotechnology, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India

Mu. Naushad Department of Chemistry, College of Science, King Saud University, Riyadh, Saudi Arabia

T. Paramasivan Laboratory for Bioremediation Research, Unit Operations Laboratory, Department of Biotechnology, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India

Soodamani Periyasamy Department of Chemistry, Anna University, University College of Engineering – Dindigul, Dindigul, Tamil Nadu, India

C. N. Peter Department of Applied Chemistry, Doornfontein Campus 2028, University of Johannesburg, Johannesburg, South Africa

A. Saravanan Department of Biotechnology, Rajalakshmi Engineering College, Chennai, India

Atul Sharma Environmental Chemistry Research Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi, India

S. K. Shukla Department of Polymer Sciences, Bhaskaracharya College of Applied Sciences, University of Delhi, Delhi, India

Sudheesh K. Shukla Department of Applied Chemistry, Doornfontein Campus 2028, University of Johannesburg, Johannesburg, South Africa
School of Environmental Science and Engineering, Shandong University, Jinan, People's Republic of China

Bhawana Singh Environmental Materials Division, CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), Nagpur, India

N. Sivarajasekar Laboratory for Bioremediation Research, Unit Operations Laboratory, Department of Biotechnology, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India

Abdelaziz Smara Laboratory of Water Treatment and Valorization of Industrial Wastes, Chemistry Department, Faculty of Sciences, Badji-Mokhtar University, Annaba, Algeria

Nazia Tarannum Department of Chemistry, Chaudhary Charan Singh University, Meerut, Uttar Pradesh, India

Cristina Trois School of Engineering, Howard College, University of Kwazulu-Natal, Durban, South Africa

Neelima Varshney Environmental Materials Division, CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), Nagpur, India

S. Vasudha Priyadharshini Laboratory for Bioremediation Research, Unit Operations Laboratory, Department of Biotechnology, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India

Swati Verma Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee, India

Natrayasamy Viswanathan Department of Chemistry, Anna University, University College of Engineering, Reddiyarchatram/Dindigul, Tamil Nadu, India

J. S. Vivek Laboratory for Bioremediation Research, Unit Operations Laboratory, Department of Biotechnology, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India

Rui Wang School of Environmental Science and Engineering, Shandong University, Jinan, People's Republic of China

P. R. Yaashikaa Department of Chemical Engineering, SSN College of Engineering, Chennai, India

Bo Yang Department of Environmental Engineering, College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen, People's Republic of China

Xu Zhao Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, People's Republic of China

Chapter 1
Environmental Issues: A Challenge for Wastewater Treatment

Meenakshi Choudhary, C. N. Peter, Sudheesh K. Shukla, Penny P. Govender, Girish M. Joshi, and Rui Wang

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Abstract In the present era, wastewater treatment is a challenging issue for living organism and biophysical environment. According to United Nation (UN) Office for the Coordination of Humanitarian Affairs (OCHA), climate change is not just a distant future treat, it is the main driver behind rising humanitarian need, and we are

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M. Choudhary
Swiss Institute for Dryland Environmental and Energy Research, Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Beersheba, Israel

C. N. Peter · P. P. Govender (✉)
Department of Applied Chemistry, Doornfontein Campus 2028, University of Johannesburg, Johannesburg, South Africa
e-mail: pennyg@uj.ac.za

S. K. Shukla (✉)
Department of Applied Chemistry, Doornfontein Campus 2028, University of Johannesburg, Johannesburg, South Africa

School of Environmental Science and Engineering, Shandong University, Jinan, People's Republic of China

G. M. Joshi
Department of Engineering Physics and Engineering Materials, Institute of Chemical Technology (ICT), Jalna, Maharashtra, India

R. Wang
School of Environmental Science and Engineering, Shandong University, Jinan, People's Republic of China

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seeing its impact. Either there is a lot of environmental issue, but wastewater treatment is one of the main environmental issues for the twenty-first century. Wastewater challenges not only depend on legislations for controlled effluent but also on socio-economic condition as well as regional characteristics. In this scenario, it is difficult to categorize a common reason to all these situations. In a note, there is a need for implementation of cost-effective and high-performance waste treatment system, and public awareness is of importance. Improper treatment of wastewater from industries and houses before disposal poses severe environmental as well as health issues to the surrounding communities. In this book chapter, we are highlighting several treatment techniques and approaches which have been developed and applied in making sure that these wastewaters are properly treated before being discharged into the environment.

Keywords Wastewater treatment · Water crisis · Environmental issue · Wastewater management

1.1 Introduction

It is very difficult for living organisms, i.e. both plants and animals, to survive without water; hence water is classified as the most essential resource for human life. Water is used extensively for many purposes which include among others drinking, agriculture, cleaning, industrial purposes, mining, etc. The quality of water is compromised by pollution caused by agricultural activities, human activities, mining, energy generation, deforestation, industries and urban settlements (Rangreez et al. 2015). Wastewater from the industries are discharged directly or indirectly into the water bodies and surrounding environment or in some cases used for irrigation purposes and, hence, need to be treated before discharge in order to save the life of aquatic animals and human health in general (Naushad et al. 2015; Ahlawat and Kumar 2009). It has been recorded that approximately 300–400 million tons of heavy metals, toxic sludge, solvents and other organic waste are being deposited into the surrounding environment by industrial plants every year worldwide (Alam et al. 2014; Xiao et al. 2015).

One of the most important raw materials used in the textile, food, paper and pulp and pharmaceutical industries are dyes. Wastewater from these industries usually contains dye residues which are not readily biodegradable. Wastewater containing these dye residues creates some negative effects on the environment especially when they enter into the water bodies. Colour hinders the penetration of light in water which in turn affects the process of photosynthesis in the aquatic system (Gupta 2009; Zhao et al. 2005). A large number of resources like chemicals, fuel and water are consumed in textile manufacturing processes leaving a large amount of waste behind. About 10–25% of textile dyes are lost during the dyeing process, and depending on the type of dye used, about 2% for basic dyes and about 50% for the reactive dye is usually discharged as aqueous effluents in different environmental sectors (Zaharia et al. 2012) leading to surface water and groundwater pollution. The loss of these dyes arises from the fact that not all of the dye binds to the fabric during the dyeing process.

Synthetic dyes can be grouped as anionic (direct acid and reactive), cationic (basic) and non-ionic (disperse) dyes (Mishra and Tripathy 1993). Due to its bright colour, water fastness, availability in different types, simple application techniques with low energy consumption (Zaharia et al. 2012) and also its ability to be applied to both natural and synthetic fibres, reactive dyes are the most commonly used dyes in the textile industry (Aksu 2005). Reactive dyes can pass through conventional treatment systems without undergoing much change, thus making its removal problematic (Anjaneyulu et al. 2005).

It is estimated that every year about 280,000 tons of textile dyes are lost in effluents from the textile industry worldwide. The amount of dissolved oxygen is decreased by the thin layer of discharged dyes that form over the surface of water bodies which in turn affects aquatic fauna (Arroyave Rojas et al. 2008). Apart from the effect of their colour, absorption of dyes on human health is also detrimental. The breakdown products of dyes through the gastrointestinal tract affect the haemoglobin, skin, lung and blood formation (Börnick and Schmidt 2006). With regard to their synthetic and aromatic nature, synthetic dyes are non-biodegradable and carcinogenic and may lead to dermatitis, allergies and skin irritation (Börnick and Schmidt 2006; Suteu et al. 2009; Zaharia et al. 2009). Hence, it is of the utmost importance to treat wastewater before discharging into the environment.

In this chapter, we are describing the concerned challenges for the wastewater treatment which is one of the very serious environmental issues nowadays. In addition we also described the possible approach to shoot out these environmental challenges. This chapter is also highlighting the photocatalyst which is very common and effective to shoot out this issue.

1.2 Waters Become an Environmental Challenge

The earth's surface is covered with about 70% of water. Water from the sea and ocean which make up about 97% of the earth's water entities is saline (i.e. contain a high amount of salt) and cannot be used for drinking, industrial and agricultural purposes. While only about 3% of the earth's water is freshwater. About 69% of this available freshwater for human and animal consumption is trapped in places like mountainous regions, Greenland, ice caps and glaciers, and only about 30% is underground which in most cases are very deep and difficult to access for uses. The only accessible water source available for human and animal consumption is less than 1% of the freshwater, and it is found in water bodies like the lakes, rivers, ponds, streams and reservoirs; hence, keeping these water bodies clean should be our utmost priority on earth for survival (Freeman 2017; Perlman 2017.) Water pollution, that is, the release of unwanted substances into the water bodies to the extent that it interferes with the functional ecosystem, is one of the major problems we are facing in the twenty-first century. The world's population is growing at ~ 80 million people per year (mppy), and this has resulted in the demand for freshwater consumption along with increase at about 64 billion metres cube per year. This breakneck in populations and urbanisation is giving rise to an increase in the amount of wastewater generated and disposed of into the environment both from the industries and human activities (Junior 2017; Karasov 2017).

The ability of countries, cities and towns to grow, attract investors and at the same time fulfil the fundamental needs of the populations and also take care of the environment properly will be in danger, if water sources and wastewaters from industries including dye-producing and dye-using industries are not well managed.

Water is one of the essential commodities on earth and a valuable facility for human advancement. All living things depend on it for survival. Approximately two-thirds of the earth is covered with water. However, human activities, rapidly growing worldwide population, advance in technology, and large demand and supply of available water to agriculture, textile industries, cities and town as well as climate change are some of the contributing factors to water scarcity (Cosgrove and Loucks 2015). Reports from the 2010 Pan African Chemistry Network revealed that the population of Africa in 2009 exceeded more than one billion with a continuous growth rate of 2.4%. Moreover, about 340 million people from this population were found to lack access to safe drinking water, while about 590 million also lack access to proper sanitation practice (Oleszczuk and Baran 2004). In addition, the 2006 United Nations Development Programme (UNDP) reports show that more than 1.1 billion people from most developing countries do not have access to water and 2.6 billion people also do not have proper sanitation practice (Pink 2006). There is, therefore, the need to improve sanitation and proper use of water to achieve more than 50% of clean water supply to meet the needs of the population. It has been estimated that by 2030, more than 3.9 billion people worldwide will experience water scarcity (West 2017). The intensity of water crises is mostly due to improved agricultural practices (use of herbicides, pesticides, fertilizers, etc.), human activities arising from the pollution of the waters, and rapid industrialisation as a result of releasing unpleasant and toxic chemicals into the environment especially the sources of water. It is, therefore, important to equip the monitoring authorities to check industrial activities on the environment so that our water bodies will be free from these harmful substances.

1.3 Water Pollution: Factors and Effect

Water pollution occurs when wastes from agricultural, domestic and industries (e.g. textile) are discharged directly or indirectly into water bodies (e.g. rivers, lakes, aquifers and groundwater) without prior filtering processes to remove harmful substances. These harmful substances (organic pollutants) can persist in the water for a prolonged period of time and are absorbed by the plants and animals in the lower chain harming the food chain of the larger living organisms (Harrison 1997; Office 2002). Therefore, nowadays water pollution is a major environmental issue, which demands regular revision and assessment of water resource policy worldwide. Recent studies reveal that water pollution is the main cause of diseases and deaths in the world (Larry 2015; Pink 2015). In China, 90% of water in the cities is polluted (China 2007), while as of 2007 about 500,000 peoples from China had no access to clean drinking water (Bank 1999). Moreover, apart from the severe water pollution problems in developing countries, developed countries also continue to struggle with increasing water pollution issues. For example, reports on assessed water quality of 45% stream, 47% lakes and 32% estuarine in the USA were classified as polluted water (Sheet 2004). The release of dye-containing wastes into the environment is undesirable and poses threats to our water bodies since the presence of the colour of the dyes affects the penetration of light and inhibits the process of photosynthesis and other biotic activities in the ecosystem. Furthermore, the colour again reduces gas solubility resulting in insufficient oxygen and activating anaerobic respiration along with suppressing aerobic organisms. The low level of dissolved oxygen also affects the bacterial growth, which lowers the breakdown of dead organic matter and the production of the corresponding nutrients (Rai et al. 2005). A number of health effects arising from water pollution such as damage to the kidney, central nervous system and reproductive system, ulceration of the skin and mucous membrane, haemorrhage and brain and liver disorder are also reported (Zhang et al. 2012). Metals associated with dyes such as Cr^{6+} when accumulated to a very high level are found to be carcinogenic and mutagenic (Anjaneyulu et al. 2005). Dyes are stable towards sweat, microbial degradation, detergents and photolysis and therefore can persist in the environment for relatively long period of time (Vilar et al. 2011). For example, hydrolysed Reactive Blue-19 has a half-life of about 46 years at pH 7 at room temperature (Soloman et al. 2009). The dissolved solids from textile effluent, when discharged, can lead to high levels of total dissolved solids (TDS) in the waters, which are harmful to vegetation and therefore prevent its utilisation for agriculture activities (Solís et al. 2012). Effects of residual chlorine from dye effluents can cause depletion of dissolved oxygen and affect aquatic life, especially aerobic living organisms. In addition, this residual chlorine may react with some aromatic compounds to produce toxic chlorinated aromatic (Merzouk et al. 2009). There are other non-biodegradable organic compounds in textile effluents, which may cause an increase in the COD of the effluent thereby disturbing the balance of the aquatic environment (Manu and Chaudhari 2002).

1.4 Nanotechnology and Environmental Issue

Nanoscience and nanotechnology are branches of engineering and science that deal with the manipulation of materials or emphasize the importance of matter on the nanometre scale (1–100 nm). Nano is a prefix applied in metric for measurements of length as nanometres, which can be used to specify the amount of a quantity such as nanoamperes (an amount of current in electricity) or nanolitres (an amount of a volume) or nanograms (an amount of mass). A nanometre is, therefore, defined as a one-billionth of a metre (1×10^{-9} m). Nanoscience is the process of studying the existence and monitoring of resources at microscopic, molecular and macromolecular scales where the properties of the synthesized composite considerably vary from those at a larger scale. Besides, it is involved with the convergence of material science, physics, chemistry and biology, which deals with the controlling and characterisation of matter on larger scales between the molecular and the micron size. Nanotechnology, therefore, is synthesizing, designing, characterisation, production and application of device, structures and systems by controlling the size and shape at the nanometre scale. In addition, it is an emerging discipline in engineering that relates the various methods from nanoscience to generate marketable and inexpensive viable products (Matsuda and Hunt 2005; Sahoo et al. 2007). Nanoparticles range in size from 1 nm to 100 nm and have large surface area compared to the volume, which makes them react very quickly than other molecules. There is intense research in nanoparticle currently because of its potential application in biomedical, environmental remediation, optical and electrical fields (Islam et al. 2015; Nabi et al. 2010). They showed great scientific interest by forming a bridge between bulk materials and atomic or molecular structures. A bulk material has constant physical properties irrespective of its size, while size-dependent properties are observed at the nanoscale. Therefore, material properties change as their size proceeds towards the nanoscale and as the proportion of atoms, the surface, becomes significant. Moreover, their high surface-to-volume ratio provides a huge driving force for diffusion at a higher temperature, while the optical properties confined their electrons and produced quantum effect (Hewakuruppu et al. 2013; Taylor et al. 2013a, b; Taylor et al. 2012). Current research into nanoscience and nanotechnology points to the fact that essential structures of materials can be tailored at the nanoscale to achieve specific properties using the tools of material science. In addition, these materials can be made effectively stronger, lighter, more reactive, more durable or good electrical conductors. Besides, nanotechnology has been found to meet the need for affordable, clean drinking water through rapid, low-cost detection of pollutants in water. It is anticipated that the applications of nanoparticles will in the future be used to treat industrial pollutants in groundwater through chemical reactions at a much lower cost than pumping the water out for treatment. One advantage of nanotechnology in terms of photocatalysis is that it offers extensively higher surface-to-volume ratio and this help decreasing the recombination of charge carrier to pave way for a chemical reaction, thereby increasing the surface area of the photocatalyst (Adams et al. 2003; Peter et al. 2018). The study of nanoparticle in recent times has generated a great interest in the field of photocatalysis due to its potential to enhance photocatalytic activity (Linic et al. 2011; Warren and Thimsen 2012). Therefore, research into nanoscience and nanotechnology has the abundant potential towards the enhancement of photocatalytic activity.

1.5 Current Approach for Wastewater Treatment (e.g. Organic Pollutant)

The treatment methods for dye removal are grouped into (i) biological, (ii) physical/physiochemical, (iii) chemical and (iv) advanced oxidation processes (AOPs). The biological method, which consists of biodegradation, bioaccumulation and biosorption, is mostly employed for removal of colour from effluents. These methods are found to be economical and environmentally friendly but cannot be used on large scale due to fluctuating effluent parameters (temperature, pH, etc.) which make them less effective. Besides, controlling the effluent parameters for optimum microbial growth is difficult (Vijayaraghavan and Yun 2008). The complex nature of dye structures coupled with its stability towards biodegradation makes biological processes ineffective under aerobic conditions. The anaerobic condition can be employed for decolourizing of the effluent, but the possible formation of aromatic amines known to be carcinogenic and mutagenic during the process is not advisable. The physical/physiochemical methods include adsorption, chemical- and electrocoagulation, membrane processes and ion exchange. The most widely used physical method for removing colour from effluents is adsorption, but this only transfers the pollutants from aqueous phase to the solid phase. Therefore, high-concentrated sludge is generated leading to handling and disposal challenges (Adewuyi 2005). Chemical- and electrocoagulation also generate large volumes of sludge during its operation causing secondary pollution, which needs additional treatment. Moreover, the large doses of chemical coagulates added to increase coagulation in chemical coagulation (for neutralisation of charges) are also not environmentally friendly (Aksu and Dönmez 2005). There is the need to add more chemicals, such as soda, ash or lime, for pH adjustment before and after treatment. It is also sensitive to temperature changes. Ion exchange methods are not often used due to lack of adaptability in its application because it works only for a narrow range of ionic dyes (Robinson et al. 2001). Moreover, the precipitate formed from cation resin recharger (H_2SO_4) and calcium from water can foul the resin beads and block the pipes in the vessels preventing effective exchange of ions (Lower 2007). When the ferrous ion in water comes in contact with air, it forms ferric ion and precipitates to ferric hydroxide which then clogs the resin beads and affects the resin efficiency (Zingaro et al. 1997). Membrane processes (microfiltration, ultrafiltration, nanofiltration, reverse osmosis and forward osmosis), when coupled with other pretreatment methods, can remove colour, inorganic ions, microbes and other organic compounds from effluents. The main drawback is the high operating pressure and sensitivity to fouling, which affect permeation and therefore need to change membranes regularly giving rise to extra operation cost (Fersi and Dhahbi 2008). They are not recommended for the removal of microorganism, some pesticides and volatile organic chemicals (VOCs) due to the membrane deterioration by bacteria (Skipton 2008). Chemicals like chlorine, chlorine dioxide and hypochlorite have been employed as oxidation agents in chemical oxidation processes. However, the formation of toxic chlorinated organic compounds due to the stability of the dye makes this method ineffective (Merzouk et al. 2009). The use of AOPs, which involves the generation of hydroxyl radical (^{-}OH), with powerful non-selective ability, has been found to be excellent treatment methods compared to the conventional methods (Elahmadi et al. 2009). The hydroxyl radical operates by attacking and mineralizing the molecules of the dye into less complex colourless molecules (CO_2, H_2O). This new set of oxidizing agents such as hydrogen peroxide (H_2O_2), Fenton's reagent (Fe^{2+}/H_2O_2) and ozone (O_3) when coupled with others and UV radiation can improve and activate the hydroxyl radical during its operation (Brillas and Martínez-Huitle 2015; Kiwi et al. 2000). Examples of such coupling are O_3/H_2O_2/UV, H_2O_2/UV/Fe^{2+}, H_2O_2/UV, O_3/UV, O_3/H_2O_2, etc. Advantages of AOPs over conventional treatments are (i) they are able to mineralize completely the dye molecules, (ii) they eliminate the formation of sludge to avoid further treatment, (iii) the non-selectivity nature of hydroxyl radical protects the versatility of AOPs in mineralizing a wide spectrum of dyes and other organic compounds (Vilar et al. 2011), and (iv) there is no occurrence of fouling because AOPs are resistant to textile effluent toxicity (Crini 2006; Singh and Arora 2011).

However, the sustainability of UV is the main challenge in this method, since UV accounts for only 4% of the solar radiation, and using UV artificial sources is expensive (Perez et al. 2002). The operational cost of AOPs is very high because a continuous input of expensive chemical or reagents is required to maintain the operation of most AOP system. In addition, AOPs require hydroxyl radicals and other reagents proportional to the quality of contaminants to be removed. Some techniques need pretreatment of wastewater to ensure reliable performance, which may require extra cost. Moreover, it is expensive to employ AOPs to treat large quantities of wastewater, and therefore such AOPs should be employed in the ultimate stage after removing a lot of contaminants through primary and secondary treatments.

1.6 Conclusion

In this chapter, we focused on the challenges for the wastewater treatment which is one of the serious environmental issues. The dangers posed on the environment by improper treatment of wastewater—wastewater from the textile industry—before discharging was highlighted in this chapter too. The nature of dyes in effluents and while they tend to stay in the environment for a longer period as well as their negative impact on the environment was discussed. Improper treatment of wastewater from industries before disposal poses severe environmental and health hazards to the surrounding communities. Several treatment techniques have been developed and applied in making sure that these wastewaters are properly treated before being discharged into the environment.

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Chapter 2
Green Nanotechnology for the Environment and Sustainable Development

Samreen Heena Khan

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Abstract With the increase in the global human population, the adequate supply of resources has become limited. The development of pollution-free technologies for environmental remediation and clean energy supplies for the sustainable growth of human society is the need of the hour. Nanotechnology can have a substantial impact on developing 'cleaner' and 'greener' technologies with significant health and environmental benefits. The applications of nanotechnology are being explored for their potential to provide solutions to manage, mitigate, and clean-up air, water, and land pollution, as well as to improve the performance of conventional technologies used in environmental clean-up. Green nanotechnology is the branch of nanotechnology that envisages sustainability through various applications.

The present chapter deals with the topics related to green nanotechnology for sustainable development. The applications of nanotechnology used to solve environmental issues by reducing the overall energy consumption during the synthesis and manufacturing process, the ability to recycle products after use, and to develop

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S. H. Khan (✉)
School of Nano Sciences, Central University of Gujarat, Gandhinagar, India
e-mail: samreen.heena.khan@gmail.com

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and use eco-friendly materials were summarized in this chapter. The sections have been divided according to the applications of green nanotechnology. The nanomanufacturing processes, green synthesis of nanomaterials, and the treatment of wastewater with reference to the principles of green chemistry have been discussed in detail. Currently, nanotechnology shows great promise to solve the sustainability issues, but it is impossible to overlook the adverse effects of nanomaterials on the environment and human health. In spite of the high performance and low cost of nano-remediation technology, advanced research is necessary to understand and prevent the potential adverse environmental impacts, i.e., ecosystem-wide impacts. The present chapter highlights the green chemistry principles influencing the life cycle of nano-products from design to disposal. The various applications and limitations of green nanotechnology have been discussed in the light of green chemistry principles for sustainability.

Keywords Green Nanotechnology · Photocatalysis · Remediation · Sustainable · Nanomaterials

2.1 Introduction

One of the biggest challenges of the present situation is to provide sustainable development for the coming generations utilizing the concepts and principles of green chemistry and green engineering to make nano-products and materials without noxious end products and to expend lifecycle thinking in all design and engineering phases (Galeazzo et al. 2014; Qu et al. 2013). Nanotechnology has the potential to use novel nanomaterials for groundwater, surface water, and wastewater remediation contaminated by heavy metal ions, organic–inorganic solutes, and a wide range of microorganisms (Kumar et al. 2017; Awual et al. 2015). At present, several nanomaterials are in the extensive research and development (R&D) stage for use in environmental clean-up and site remediation due to their unique activity toward nondegradable contaminants. Green manufacturing is the most efficient way to reduce and eliminate the release of toxic pollutants in soil, water, and air environments (Allen and Shonnard 2001). The use of nano-adsorbents can effectively remove organic pollutants, dyes, and dye effluents from contaminated water, such as clays, zeolites, metals, metal oxides, polymeric membranes, porous nanofibers, and zero-valent iron (West and Halas 2000; Seil and Webster 2012). Semiconductor-based photocatalysts are used in the advanced oxidation processes (AOP) for the degradation and mineralization under irradiation (natural & artificial) of toxic organic contaminants into environmentally friendly compounds (Tratnyek and Johnson 2006).

Nanoscience, considered as an emerging field, provides an informative framework to study the applications and implications of green chemistry in a broader and safer way. As compared to the previous remediation technologies, nano-remediation involves the overall reduction of contaminations (Bardos et al. 2015). Nano-based technologies can be used for the prevention, mitigation, and minimization of damage caused to human health and the environment (Hood 2004). The use of the green nano-manufacturing process involves the development of low-cost, nontoxic, and multifunctional efficient nano-products without generation of hazardous end products (Dornfeld et al. 2013). At present, nanotechnology is making substantial development in technologies for the protection of the environment, and it is being explored for its potential to provide new solutions to managing and eliminating air, water, and land pollution. It is also aims to improve the performance of conventional technologies used in clean-up efforts (Shapira and Youtie 2015).

The application of nanotechnology for in situ remediation provides a fast and cost-effective remediation technology solution (Diallo et al. 2013). Nano-based remediation technology has the potential not only to reduce the overall costs of remediation of contaminated sites but also to reduce clean-up time, eliminate the need for disposal and treatment of contaminated soil, and reduce the risk of contaminant to near zero (Gil-Díaz et al. 2016; Glavič and Lukman 2007). Owing to their unique activity toward recalcitrant contaminants, nanomaterials are being explored in advanced research and development for their use in environmental clean-up and on-site remediation (Zhang 2003; Smol and Stoermer 2010). Recently, many different nanomaterials have been evaluated for use in nano-remediation, such as nanoscale zeolites, metal–metal oxides, carbon nanotubes, dendrimers, noble metals, metal–polymer doped nanoparticles, etc. (Bardos et al. 2015; OECD 2011c). Nanotechnology has also contributed to reducing the presence of nonaqueous phase liquids (NAPL), in addition to the surface and groundwater remediation (Dreher 2004) by utilizing the nanomaterial oxide in situ to clean-up heating oil spills from the underground oil tanks (Fagan et al. 2013; Deif 2011; Rusinko 2007).

As compared to the previous remediation technologies, the nano-based approaches proved an efficient method for the reduction of overall contaminant levels (Sharma and Sanghi 2012). Green nanotechnology revolves around the use of nanotechnology applications for the development of eco-friendly products and processes (Dornfeld et al. 2013). The major objective of these technologies is the development of environmentally friendly designs that help to reduce the environmental and health implications by replacing the present applications (Maksimović and Omanović-Mikličanin 2017).

2.1.1 Definition

Nanotechnology is the major research area that involves the things working on the nanometer (nm) scale. It plays an important role in the expansion of innovative technologies for the design and development of new products, replacing the existing production equipment and formulating new chemicals and materials with enhanced performance (Leach et al. 2002; Dhingra et al. 2010).

The aim of the chapter is to highlight the concept of green nanotechnology under the light of green chemistry and sustainability. Green nano involves the principles of green chemistry, so it is very important to understand "*Green Chemistry*" and nanotechnology first. The purpose of green chemistry is to reinvent the use of chemicals to be safer and more efficient (Andraos 2005). At this point, the sustainability movement interferes in nanotechnology and the term sustainable and green chemistry are thoroughly used (Schulte et al. 2013). Table 2.1 provides the general definitions of the commonly referred to terms.

Green nanotechnology has two goals, *process and product*, which involve use of multifunctional nanomaterials for the renewable energy generation, nano-sensors for detecting and monitoring the pollution, green packaging, semiconductor photocatalysis for effective environmental remediation, and a novel membrane for more efficient treatment and purification of wastewater (Ran et al. 2008; Wei Guo 2011). The principles of green chemistry along with the sustainability help to recognize many opportunities for new research in this field (Anastas and Warner 2000). Green chemistry confirms that nanotechnologies lessen the unintentional hazards by providing the vision about the implications of the new technologies. When considering the implications and applications of recent technologies, green chemistry stands apart from other technological trends that focus entirely on products and processes (OECD 2011a).

Green nanotechnology is undoubtedly the most important branch of nanotechnology, utilizing the 12 principles of green chemistry for various potential applications. Being an emerging area, nanoscience offers promising opportunities to the principles of green chemistry to create sustainability and protect and promote occupational safety and health during the product manufacturing and process application (Matos et al. 2010; Anderson et al. 2010). After understanding the concept of green nano for sustainable development, the focus has been shifted toward the different application areas that are relevant to greener growth and sustainability (Lazaro et al. 2013; Mulvihill et al. 2011). Figure 2.1 presents the six application areas of green nanotechnology.

In the above-mentioned areas, nano-based applications offer potential benefits, such as lower toxicity, lower cost, higher efficiency, reduced complexity, and reliability. It also offers the opportunity to overcome the adverse effects even before

Table 2.1 General definitions

Term	Definition
Nanotechnology	It is the branch of technology that deals with dimensions 1–100 nanometers, especially the manipulation of individual atoms and molecules
Green nanotechnology	The technology used to develop clean technologies in order to minimize health and potential environmental risks. It involves the use of nano-products and the nano-manufacturing process
Green chemistry	It is the design of *chemical* products and processes that diminish and eradicate the use and generation of toxic substances. It is applied throughout the life-cycle of a *chemical* product, including its design, manufacturing, use, and ultimate disposal (end-of-life)
Sustainability	*It is the development* that fulfills the needs of the present, without compromising the ability of future generations

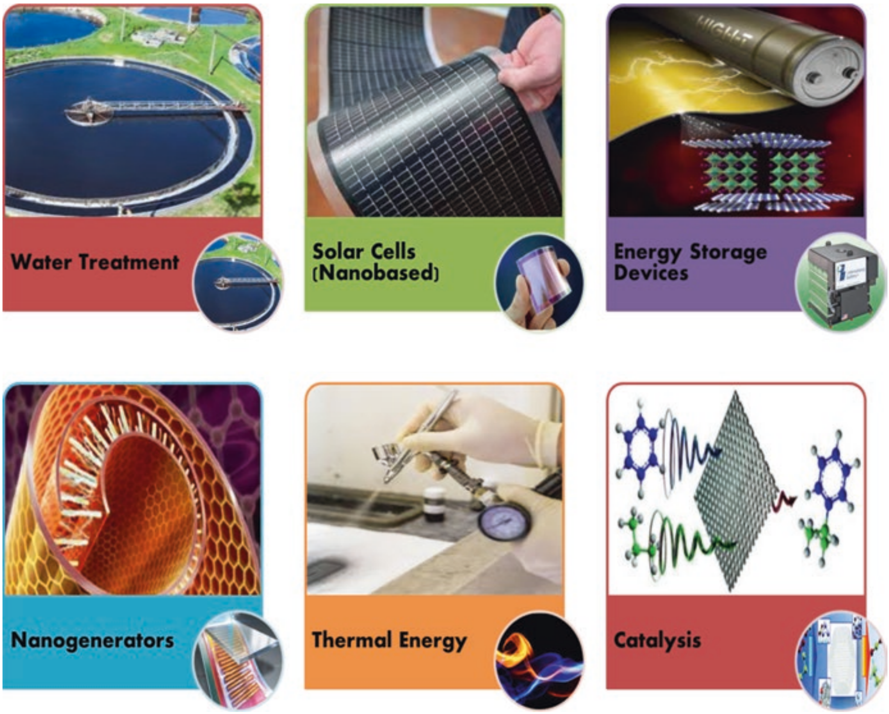


Fig. 2.1 Major research areas of green nanotechnology

they occur (Owen and Depledge 2005). Green nanotechnology can competently influence the design of nanomaterials and products by eliminating/minimizing pollution right from the synthesis, by life-cycle assessment, by estimating and mitigating where environmental impacts might occur in the product chain, and by designing nontoxic nanomaterials and utilizing them for the solution of the existing environmental problems (Som et al. 2010; Iavicoli et al. 2014). Apart from the obvious areas, using nanomaterials in the field of photocatalysis (Hashimoto et al. 2005), solar cells (Fujihara et al. 2007), fuel/bio-fuel cells (Ramsurn and Gupta 2013), and applications of green nanotechnology also involves cleaner production and processes, such as synthesis of nanoparticles using greener methods (biological synthesis). Further, recycling of industrial waste materials into nanomaterials by turning diesel soot into carbon nanomaterials, flyash into silica, alumina, and iron oxide nanomaterials is also included in the applications of green nano (Matos et al. 2010; Biju et al. 2008).

It is a general perception that nanotechnology will develop greener and cleaner technologies for the benefit of the environment and will involve diverse areas of waste. The very first idea about the concept of green nanotechnology was given by the ACS Green Chemistry Institute in partnership with the Oregon Nanoscience and Microtechnologies, addressing the challenge and opportunities involving green nanotechnology. Scientists and engineers assume that the safest future for the advancement in nanotechnology for sustainable development can be achieved by using the principles of green chemistry (Anastas and Kirchhoff 2002). There are 12 principles of green chemistry that green nanotechnology revolves around. The application of green chemistry involves the designing of processes and products that eliminate toxic substances from the beginning to the end of a chemical's life-cycle (Tang et al. 2005). Green nanotechnology revolves around the principles of green chemistry and green engineering and emphases them through unique effects that occur in nanoscale materials.

Before discussing green nanotechnology, it is of utmost importance to understand the basic *"Principles of Green Chemistry"* that were posted by the USEPA. Green chemistry, sometimes referred to as sustainable chemistry, involves the design, development, and production of chemical products and processes that can reduce the generation risk of toxic waste and hazardous end products during the manufacturing process (Naidu et al. 2008). It is noteworthy that the principles of green chemistry completely apply to green nanotechnology and nano-manufacturing processes. The 12 principles of green chemistry are given in Table 2.2.

The principles of green chemistry can be applied to produce cleaner, safer, and more sustainable nanomaterials and manufacturing processes. On the other hand, a principle of nanoscience along with green chemistry eases the syntheses of bulk and makes nanomaterials more environmentally friendly (Jahangirian et al. 2017; Anastas and Warner 1998a, b). Thus, green nanotechnology is closely interconnected with both the principles of green chemistry and green manufacturing.

In this chapter, the concepts of green engineering/green chemistry and green manufacturing are explored with a special reference to nanoscience. As the vast majority of the research in this area has been focused on the development of greener processes and approaches, this chapter will be mainly focused on the synthesis and applications of nanomaterials. Figure 2.2 demonstrates the pictorial representation of the principles of green chemistry involved in the green synthesis process.

Nanotechnology offers immense hope for the development of new technologies that are greener and more sustainable than the present technologies. Almost all the major sectors have a significant impact on the advancement of nanotechnology involving the incorporation of nanomaterials in the products and processes. The synthesis of nanomaterials for these very products uses many chemicals and chemical manufacturing processes. Owing to that, the synthesis process results in the production of toxic end products causing adverse health and environmental implications (Virkutyte and Varma 2013). The main aim behind green nano is the development of nonhazardous protocols for the products syntheses and other associated processes. The major goal is the minimization of the risks and hazards associated with the nanomaterial synthesis as the release of toxic nanomaterials give rise to the nanotoxicity issues (Fischer and Chan 2007). Thus, the green nanoproducts are those nanomaterials that are synthesized using the principles of green chemistry and directly and indirectly used for environmental applications, such as environmental remediation, treatment of wastewater, etc.

Table 2.2 General principles of green chemistry (Anastas and Warner 1998a, b)

S. No.	Principle	Description
1.	Prevention	Better to prevent waste than to treat or clean up waste after it has been created
2.	Atom economy	Synthesis methods should be designed to maximize the incorporation of all materials used in the process into the final product
3.	Less hazardous chemical syntheses	Wherever practicable, synthesis methods should be designed to use and generate substances that possess no toxicity to human health and the environment
4.	Designing safer chemicals	Chemical products should be designed to affect their desired function while minimizing their toxicity
5.	Safer solvents and auxiliaries	The use of auxiliary substances, such as solvents, separation agents, etc., should be made unnecessary wherever possible and innocuous when used
6.	Design for energy efficiency	Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthesis methods should be conducted at ambient temperature and pressure
7.	Use of renewable feedstocks	A raw material should be renewable rather than depleting whenever technically and economically practicable
8.	Reduce derivatives	Unnecessary use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes, etc., should be minimized and avoided if possible because such steps require additional reagents and can generate waste
9.	Catalysis	Catalytic reagents (as selective as possible) are superior to stoichiometric reagents
10.	Design for degradation	Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment
11.	Real-time analysis for pollution prevention	Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances
12.	Inherently safer chemistry for accident prevention	Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires

As we know, the processes and product applications of green nano comprise synthesizing nanomaterials using environmentally friendly methods and using the as-synthesized nanomaterials in environmental clean-up processes making the whole concept of green nano even more feasible and acceptable. The best example of synthesizing nanomaterials using a greener approach is by biological synthesis methods using plants, microbes, etc. (Ramya and Subapriya 2012). Also, during chemical synthesis, replacement of organic solvents with less toxic and harmful solvents reduces the toxicity manifolds. Additionally, in order to come under the green tag, the processes and products must be considered under the lifecycle framework.

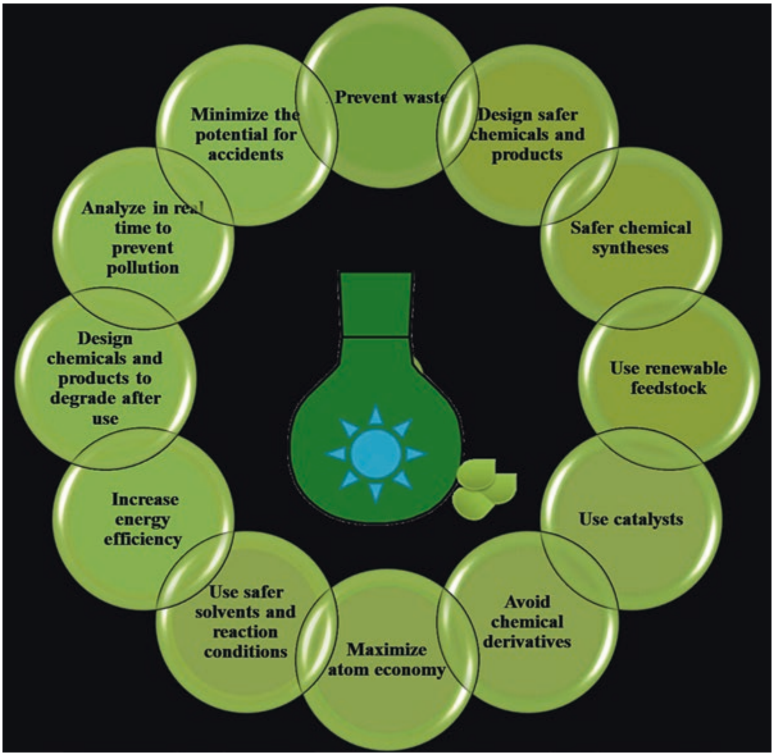


Fig. 2.2 Pictorial representation of the principles of green chemistry in green synthesis

A large number of outstanding reviews have already been published on the synthesis and functionalization of nanomaterials; hence, this chapter has focused on the aspects of products and processes relevant to green chemistry instead of focusing on the details of synthesis processes.

2.1.2 Green Nanotechnology

As the term green suggests there is something environmentally friendly here. Green nanotechnology involves the development and application of products in an environmentally friendly way, whereas green chemistry is defined as the "the utilization of the twelve principles that reduces and eliminates the use or generation of hazardous substances in the design, production, and application of chemical products and processes" (Karn and Bergeson 2009). The principles of green chemistry, defined by Anastas and Warner (1998a, b) and given in Table 2.1, are applied nowadays for the production of a wide range of chemicals with the aim of reducing hazards to health and the environment, minimizing wastes, and preventing pollution. The application of the 12 principles of green chemistry has decreased the consumption of toxic solvents and reagents manifold, enhanced the design of products for the end-of-life, and enhanced the material and energy efficiency of chemical procedures. The application of these principles of green chemistry to nanoscience will ease the synthesis and processing of safer and greener nanomaterials (Anastas and Eghbali 2010). Green nano involves the application of green chemistry to the design and development of nanomaterial production methods (small and large scale) and the application of nanomaterials in various areas (Albrecht et al. 2006). It also aims to provide knowledge about the properties of nanomaterials with reference to the toxicity issues and the design of multifunctional nanomaterials that can be used in high capacity products, which can pose a threat to human health and the environment (Tobiszewski et al. 2010). Most importantly, it attempts to develop the synthesis/methods that can eliminate the need for harmful chemicals while enhancing the efficiency of these existing synthesis methodologies (Varma 2014). It also provides the outlines for assuring that the as-synthesized nanoproducts are safer by accessing the ecological risks and hazards with reference to the design. Further, it seeks the application of nanotechnology that has a broader societal benefit by decreasing the adverse impact on health and the ecosystem. Thus, green nano starts with the development of materials, their processing, and application, throughout the life cycle, right from the beginning from the selection of raw material to the end of life (safer release to the environment) (Smith 2011). Figure 2.3 shows the benefits of green nanotechnology.

Fig. 2.3 Green nanotechnology

2.2 Application of Green Chemistry Principles to Nanoscience

Nanomaterials have a high surface to volume ratio and tunable properties make them efficient for a wide range of applications from healthcare to environmental remediation (Klabunde and Richards 2009). Nanomaterials are almost everywhere due to their multifunctionality and properties (Lue 2007). The applications of nanotechnology are growing day by day, promising environmental benefits, such as nanocatalysts for environmental remediation, thermo-electric materials for cooling-down without the use of refrigerants, efficient photovoltaic, lightweight nanocomposite materials for vehicles, mini devices to reduce the consumption of material, and nanosensors, which eliminate the need of wet chemical analysis. Nanosensors are fasters and their lower detection limits make on-site detection possible (Liang and Guo 2009). The new nanotechnologies are beneficial yet possess little harm to human health and the environment; therefore, it is necessary to design and develop the green nanomaterials and their synthesis methods (Schmidt 2007). First, the nano-manufacturing process has been discussed in the light of green chemistry, and later the application part has been discussed.

It is a known fact that nanomaterials have rich structural diversity, providing a wide opportunity to tune the physical, chemical, optical, and toxicological properties. During experimental design and analysis, extreme care should be taken as the complexity and diversity of nanoparticles can alter the toxicity related issues (Maynard 2006). Significantly, the use of different synthesis methods for the production of similar products means the difference in the methodology and reaction routes leads to a difference in product purity, quantity, intermediate, and end product. Also, the synthesized nanomaterials should be characterized in detail by known particle size, shape, size distribution, surface area, morphology, solubility, crystallinity, physical, chemical, optical, and electronic properties (Rawle 2017; Montone et al. 2015). The utilization of these well-characterized nanomaterials allows accurate biological and ecological impact assessment (Ikhmayies 2014). The principles also focused on the impact of nanomaterials that may be released to the environment after the application. Thus, the design of material should also focus on the very aspect that it should reduce harm to the environment by using environmentally friendly materials (Hutchison 2008). It also aims to design such materials that are safer and radially degrade into the environment without generating toxic intermediates and hazardous end products (Colvin 2003). To implement the principles, the fate and life cycle assessment of the nanomaterial is needed. Various short-term and long-term effects of the nanomaterials in the water, soil, and air should also be considered in view of human health (Milburn 2012) as the prolonged persistence of nanomaterial in the environment gives rise to nanotoxicity related issues. Nanotoxicology is intended to describe the toxicological properties of an engineered nanomaterial to decide whether and to what extent nanomaterials pose a threat to the environment and human health (Hoet et al. 2004). In terms of their fate in the human body and in the environment, the size of nanoparticles and lack of detection method presents a huge drawback in the context of identification and remediation (Linkov et al. 2011; Maynard et al. 2006). It is noteworthy that not all the nanoparticles are toxic to the environment; it depends on their concentration, dosage, and exposure rate (Martin et al. 2008; Krishnaswamy and Orsat 2017). Over the past decades, the fate, transport, and toxicity of engineered nanomaterials have been a major focus of environmental health and safety research throughout the globe. The basic and fundamental properties concerning the fate of nanomaterials are not well understood due to the lack of research studies (Klaine et al. 2008). The rapid consumption, usage, and production of nanomaterials ultimately lead to environmental exposure (Khan et al. 2015; Dhawan et al. 2009). Also, less is known about the eco-toxicological concerns and chronic effects of nanomaterials to date. Green nanotechnology focuses on various processes as summarized in Fig. 2.4:

The major application of Green Nanotechnology involves:

Fig. 2.4 The main focus area of green nanotechnology

2.2.1 Nanomanufacturing

The application of the principles of green chemistry in the nanomanufacturing/nano synthesis process is an emerging area aimed at sustainable development. It has gained worldwide attention in recent years due to its potential for designing multi-functional, energy efficient, and nontoxic synthesis routes (Şengül et al. 2008). It is associated with the chemicals, reagents, and solvents used during the preparation and synthesis methods. This section will focus on the synthesis routes of nanomaterials and nanoproducts with special attention to the significant environmental impacts (Chen and Schluesener 2008). All the nano-products must proceed via the various development stages to produce the particles, materials, and devices in the nanoscale dimension. A life-cycle assessment analysis checks the manufacturing of a nanomaterial and also its fate after the release in the environment up to its end-of-life (Steinfeldt 2014). The newly developed materials are expected to (a) possess high surface functionality, (b) exhibit size-dependent properties, and (c) incorporate a wide range of material and elemental compositions (Dahl et al. 2007). The assessment of these materials, before their acceptance in the commercial front, presents an opportunity for reducing the negative impact of the material, which is a must. The production of a highly precise, low waste generating method for the nanomanufacturing process will be essential for the commercialization of these products.

Green chemistry also provides the platform to increase the public perception of nanotechnology, as the present approach is comparatively easy to understand and useful to convey the responsible attitude toward the expansion of green nanotechnology (Fleischer and Grunwald 2008). That is the reason green chemistry can play the pivotal role in the growth of nanotechnology with the aim of providing the maximum benefit of these products to society (Eckelman et al. 2008). The advantages of green nanomanufacturing are as follows:

1. Production of relatively safer and greener nanoproducts
2. Eliminates the necessity of hazardous chemicals and solvents for the purpose of synthesis
3. Comparatively cheaper and environmentally friendly
4. No toxic end product
5. Requires fewer manufacturing and safety controls for the production.

Nanomanufacturing processes are widely associated with human health and environmental impacts (Asmatulu et al. 2012). It is important to evaluate nano-products for their green approaches, incorporating risk analysis and life-cycle assessment using the sustainable manufacturing approaches and employing green chemistry alternatives are the possible solution (Hutchison 2016, USEPA). Basically, for nanomaterial manufacturing, the widely used approaches are bottom-up and top-down techniques (Cao 2004; Chen and Mao 2007).

(a) ***Top-down approach:*** Reducing the material from bulk to the nanoscale. It is preferred to synthesize nanomaterials by templating.

(b) ***Bottom-up approach:*** Synthesis of organic/inorganic materials into nanostructures starting from the atom level to the nanoscale by self-assembly.

The top-down process involves the physical methods of nanomaterial syntheses, such as lithography, milling, and etching (Yadav et al. 2012). The top-down approaches start with micro-systems and miniaturizes them to the nanoscale; through grinding, it cut downs the larger material until it reaches the nanoscale dimensions (Rao et al. 2006). On the other hand, bottom-up approaches assemble the matter at the atomic scale via growth and nucleation using a precursor by means of chemical reactions, such as sol-gel, self-assembly, etc. (Biswas et al. 2012). Top-down approaches are more common compared to bottom-up for the synthesis of nanomaterials due to the ease and accessibility of use (Varma 2014). However, at the same time, it is also supposed that top-down techniques are more waste-generating compared to the bottom-up techniques. Thus, the bottom-up techniques are the ultimate tools for sustainable production as they offer the customized design of reaction, methodology, and size- and shape-controlled synthesis at the molecular level by reducing unintended waste (Bergeson and Auerbach 2004). Table 2.3 summarizes the general methods of nanomanufacturing with examples.

The nanomaterials synthesized using the above-mentioned methods are commonly referred to as engineered nanoparticles (ENPs). Nanomaterials can be classified as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) (Amin et al. 2014; Nakagawa et al. 2013). Many of the nanomanufacturing processes have low product yield causing low material efficiency leading to the generation of excessive waste. Also, some of the synthesis methods have the potential to cause unwanted human health effects (acute and chronic) due to the accidental release of nanomaterials in the environment. The examples of nanomaterials are summarized in Fig. 2.5.

The nature of these ENPs and their use gives convincing reasons for utilizing the principles of green chemistry for the development of new nanomaterials and their applications (Savolainen et al. 2010). The production of any nanoproduct requires high energy consumption, hazardous chemicals, low material conversion, and wasteful and repetitive purification; thus, there are several other ways to develop greener processes for the synthesis of nanomaterials (Gladysz 2001). The greener synthesis of nanomaterial attracts attention worldwide. There are several benefits to the green synthesis of nanomaterial over the chemical based synthesis. Through green synthesis, highly efficient, multifunctional, and less hazardous synthesis of nanomaterials can be achieved producing a higher number of particles in less time under mild reaction conditions (Schwarz 2009). Nanotechnology research can overcome the need for hazardous chemicals during the nano synthesis process through the following suggested ways:

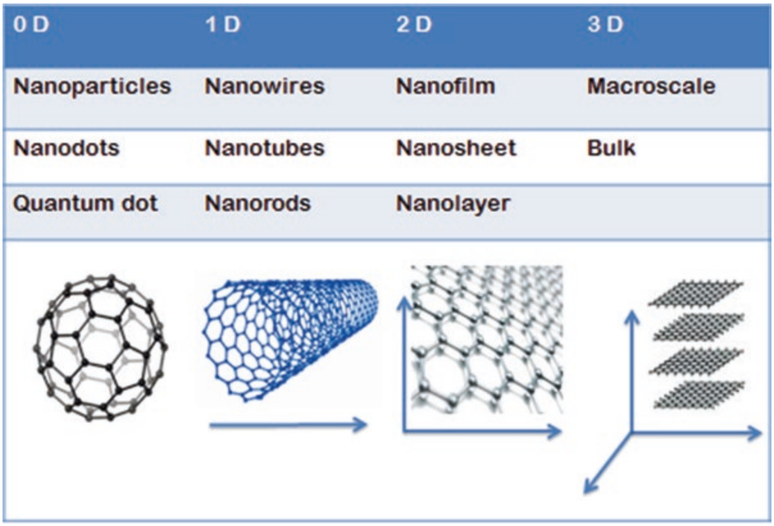
(a) Bottom-up synthesis of novel nanocatalyst (at atomic or molecular level),
(b) Molecular self-assembly as the basis of new materials,
(c) Adding information to molecules for developing new molecules,
(d) Developing nanomaterials in the micro-reactors.

Table 2.3 Common nanomanufacturing techniques

Bottom-up	Top-Down
Self-assembly	***Physical milling***
Langmuir–Blodgett self-assembly	Ball milling
Electrostatic self A	Mechanical milling
SA monolayers (SAMs)	Cryomilling
	Mechanochemical
Vapor-phase deposition techniques	
Molecular beam epitaxy (MBE)	***Electrospinning***
Plasma-enhanced chemical vapor deposition	
Atomic laser deposition	***Etching***
Pulsed laser deposition	Dry etching
Evaporation	Plasma etching
Sputtering	Reactive ion etching
Vapor phase epitaxy	Wet etching
Nanostructured material synthesis techniques	***Lithography***
Flame synthesis	Photolithography
Arc deposition	E-beam lithography
Laser ablation	Immersion lithography
Evaporation	X-ray lithography
	Extreme UV lithography
Liquid phase synthesis techniques	Focused ion beam lithography
Sol-gel method	Nanoimprint lithography
Sonochemical synthesis	Soft lithography
Solvothermal synthesis	
Microwave-assisted synthesis	
Chemical precipitation	
Electrodeposition	
Reverse micellar synthesis	
Biological synthesis	
Plants	
Bacteria	
Fungus	
Plant wastes	

2.2.2 *Green Synthesis of Nanomaterials*

Green synthesis, using the principles of green chemistry, is a new platform to design novel nanomaterials that are nonhazardous to human and environmental health and has the extensive potential to revolutionize large-scale nanomanufacturing processes (Duan et al. 2015; Wang et al. 2012). These greener nanomaterials have wide possibilities in the field of nanomedicine as novel drug carriers, etc., in the near future (Nath and Banerjee 2013). Greener synthesis of nanomaterials sets the



0 D	1 D	2 D	3 D
Nanoparticles	Nanowires	Nanofilm	Macroscale
Nanodots	Nanotubes	Nanosheet	Bulk
Quantum dot	Nanorods	Nanolayer	

Fig. 2.5 Examples of 0, 1, 2, and 3D nanomaterials

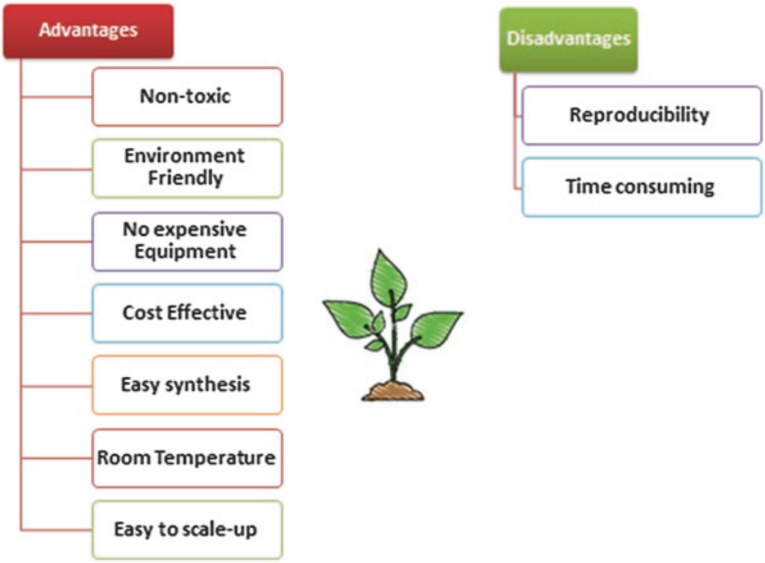


Fig. 2.6 Advantages and disadvantages of green synthesis

benchmark for the development of cleaner, safer, and sustainable nanoproducts and nanomaterials (Gawande et al. 2013). Figure 2.6 presents the advantages and disadvantages of using green synthesis processes.

The basic principles of green chemistry are the utilization of nontoxic, biodegradable, cost-effective resources and energy efficient reactions. The nanomaterials synthesized using plants, microbes, and other natural resources are commonly termed green synthesized nanomaterials. Some chemical methods also qualify for the green chemistry based synthesis methods; however, utilization of all natural products for the synthesis of nanomaterials has gained widespread attention in the nanomanufacturing area (Albrecht et al. 2006). It has been reported in the various literature that the nanomaterials synthesized using green synthesis methods are similar to their chemical counterparts and have similar efficiency. The green syntheses approaches of nanoparticles are easier, cheaper, more efficient, and eco-friendly compared to chemical or microbe-mediated synthesis. The chemical synthesis method involves the use of toxic solvents, high pressure, energy, and high-temperature conversion. On the other hand, microbe mediated syntheses are not feasible at large scale due to their lab maintenance. It is also possible to alter the properties of nanomaterials by controlling the reaction conditions, such as temperature, pH concentration, etc., in a similar way to the chemical synthesis (Vigneshwaran et al. 2006). The major applications of these greener nanomaterials lie in nanosensing, nanomedicine, nano-therapeutics, energy storage, and so on. Most importantly, greener synthesis approaches paved the way for safe and sustainable nanotechnology (Yoshida et al. 2011). Many challenges and issues are associated with green nanotechnology but that does not reduce the potential of the green and sustainable approach. Figure 2.7 shows the general methodology of green synthesis of nanomaterials.

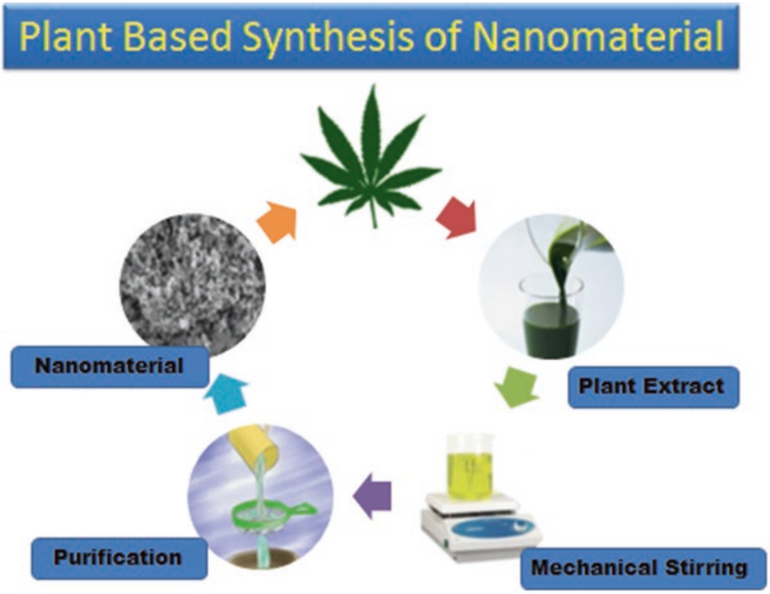


Fig. 2.7 General methodology of green synthesis

A variety of multifunctional green nanomaterials with definite composition, size, morphology, and crystallinity have been synthesized by different methods, and their potential applications have been explored. Green synthesis of nanomaterials using plants is actually a type of bottom-up approach involving oxidation and reduction as the main reaction (Sangeetha et al. 2011; Raveendran et al. 2003). The extract of the plant contains several primary and secondary metabolites, i.e., alkaloids, flavonoids, phenolic acid, and terpenoids. These compounds are responsible for the reduction/conversion of bulk into nanoparticles (Vijayakumar 2013; Makarov et al. 2014). These metabolites are mainly responsible for the redox reaction for the synthesis of eco-friendly green nanomaterials. After reviewing the literature, it was found that the synthesis phase is the major contributor to the life cycle impact of the nanomaterials as at this stage toxic waste is more prone to generate (Nune et al. 2009). Less transparency, large inconsistencies in data collection, and different methodologies were also stated by many researchers. Table 2.4 summarizes the plants used for the synthesis of different nanoparticles.

Table 2.4 Plants used for the synthesis of different nanoparticles

Plant	Nanoparticle	Size (nm)	Shape	Plant part	References
Alovera	In_2O_3	5–50	Spherical	Leaf	Maensiri et al. (2008)
Acalypha indica	Ag, Au	10–30	Spherical	Leaves	Krishnaraj et al. (2010)
Alternanthera sessilis	Ag	40–50	Spherical	Whole	Niraimathi (2012)
A. *maxicana*	Ag	20–50	Spherical	Leaves	Singh et al. (2010)
Artemesia *nilagirica*	Ag	70–90	Spherical	Leaves	Song and Kim (2009)
Andrographis paniculata	Ag	65–90	Spherical	Leaves	Suriyakalaa (2013)
Azadiricta *indica*	Ag	10–30	Spherical	Leaves	Tripathy (2010)
Boswellia serrata	Ag	7–10	Spherical	Gum	Kora et al. (2012)
Cassia fistula	Au	55	Spherical	Stem	Daisy and Saipriya (2012)
Caria *papaya*	Ag	15	Spherical	Fruit	Jain (2009)
Citrus sinensis	Ag	35	Spherical	Peel	Kaviya (2011)
Citrullus colocynthis	Ag	5–80	Triangle	Callus	Satyavani (2011)
Cinnamon *zeylanicum*	Ag	45	Spherical	Leaves	Sathishkumar (2009)
Dillinia *indica*	Ag	11–25	Spherical	Fruit	Singh et al. (2013)
Euphorbia prostrata	Ag	52–55	Rod	Leaves	Zahir and Rahuman (2012)
Mentha *piperita*	Au	90–150	Spherical	Leaves	MubarakAli (2011)
Mirabilis jalapa	Au	100	Spherical	Flowers	Vankar and Bajpai (2010)
Tinospora *cordifolia*	Ag	35	Spherical	Leaves	Jayaseelan (2011)
Withania somnifera	Ag	5–40	Irregular	Leaves	Nagati et al. (2012)
Melia azedarach	Ag	80	Irregular	Leaves	Sukirtha (2012)

There is a day by day increase in the demand of these nanoproducts, according to an estimate by The Royal Society the total production of nanomaterials annually may exceed 100,000 metric tons worldwide by the end of 2020. Thus, the development of sustainable alternatives for the novel synthesis and production methodologies is the urgent need of the hour to overcome the associated risks (Iravani 2011). It is a fact that every country that is associated with the synthesis and use of nanomaterials are very much aware of their potential risks and toxicity, though no specific regulations have been implemented regarding the use of nanomaterials so far (Science Policy Council 2005; Davis 2007; Nel et al. 2006). However, the US-EPA permits a limited production of new nanoscale material under the Toxic Substance Control Act. There is an urgent need for the pioneering countries, such as Japan, the USA, and European Union, to implement regulations on toxic synthesis approaches and the hazardous products. The nanomanufacturing processes associated with negative human and environmental impacts should be thoroughly accessed while evaluating nanomaterials for their *greenness* for sustainable development (Lu and Ozcan 2015). Figure 2.8 shows the plant-mediated nanoparticles and their applications.

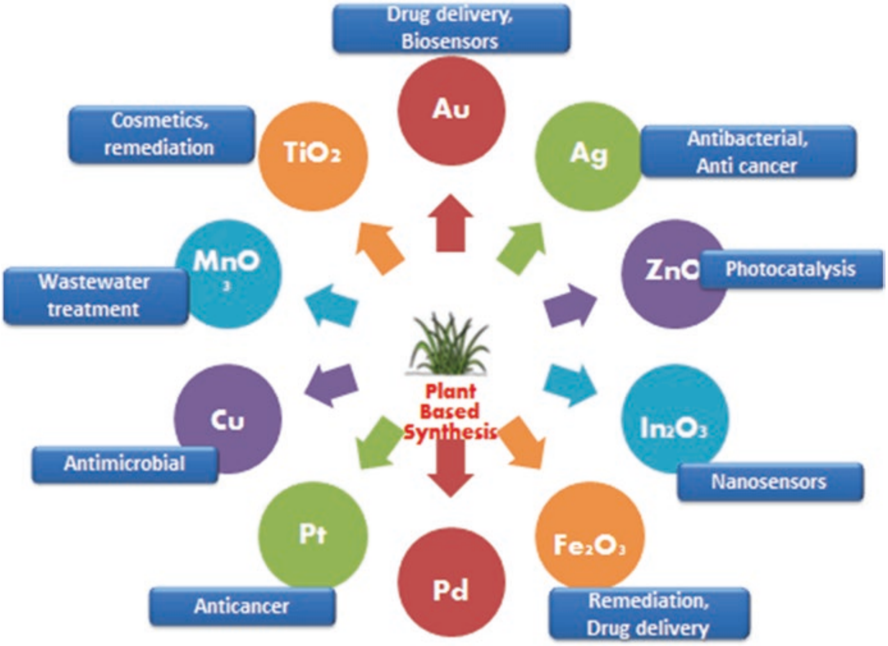


Fig. 2.8 Green synthesized nanomaterials and their applications

2.2.3 Wastewater Treatment Using Nanomaterials

The availability of clean and safe drinking water is a global challenge. Water and wastewater treatment methods are chemically intensive as well as costly and harmful to the environment to a certain extent (Naushad et al. 2016). The conventional treatment technologies require high capital input, a large area, and high maintenance costs, and they just transfer the pollutants from one phase to another, rather than completely degrading them into an environmentally friendly end product (Naushad et al. 2013; De Kwaadsteniet et al. 2011). This necessitates an alternative technology for the treatment of wastewater in a greener and more sustainable way. At present, many physicochemical methods, such as carbon adsorption, distillation, ion-exchange, reverse osmosis, and nanofiltration, are used for the purification of wastewater (Göbel et al. 2007; Clara et al. 2005). Major drawbacks associated with these methods include membrane deformation, high cost, handling, sludge formation, and disposable problems. On the other hand, non-biodegradable pollutants pose a serious threat as the majority of these pollutants require a high priority treatment (Khulbe et al. 2012). This necessitates an advanced, greener, more cost-effective method for wastewater treatment. Figure 2.9 shows the conventional and advanced wastewater treatment technologies.

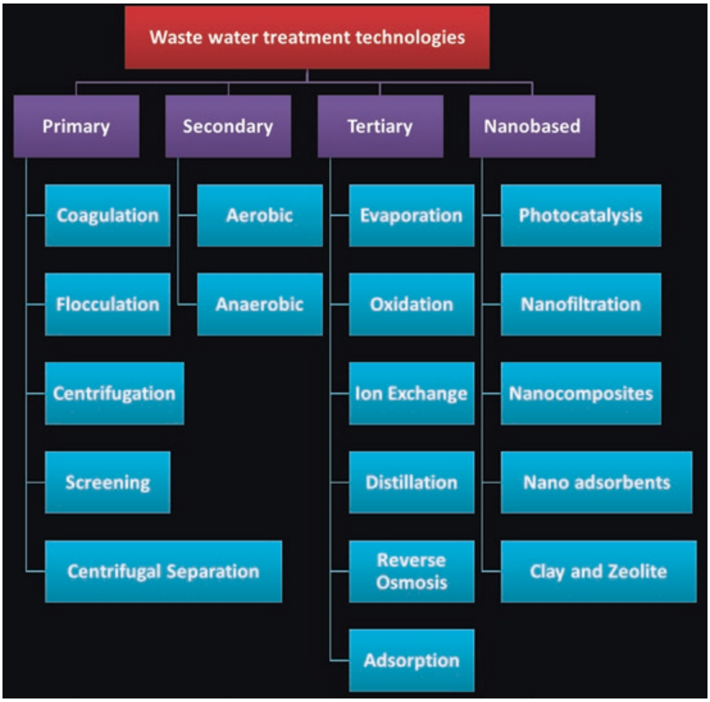


Fig. 2.9 Conventional wastewater treatment technologies

Nanotechnology provides the solution to the existing problem. Nano-based catalysts, adsorbents, and membranes can create eco-friendly solutions to wastewater treatment (Tiwari et al. 2008). Nanomaterials have gained widespread attention in the field of environmental clean-up and remediation due to their higher surface-to-volume ratio (Diallo and Brinker 2011). The other specific changes in their physical, chemical, and biological properties developed owing to their size are also an added advantage (Theron et al. 2008). Research is underway for the development of novel nanomaterials with increased efficiency, selectivity, and capacity for the treatment of wastewater. There are several benefits of using nanomaterials due to their higher surface reactivity and surface-to-volume ratio (Brame et al. 2011). Nanotechnology for water purification plays an important role in providing global water purity and security. The application of nanotechnology for the treatment of wastewater could be summarized under the following points:

(i) By nanoscale filtration techniques, such as nanofiltration using membranes,
(ii) By nano-adsorbent materials, such as sorbents, nanoclays, zeolites,
(iii) Nanophotocatalysis using nano-sized semiconductor material for environmental remediation,
(iv) Nanocomposites, such as metal–polymer nanocomposites for various applications,
(v) Nanomaterials for heavy metal remediation,
(vi) Metal and metal oxides for the removal of deadly microbes from the water.

Many research studies indicate that nano-based remediation technologies will be safer, more economical, and more efficient than the conventional techniques. Nanomaterials can be used for the sensing and detection of pollutants, remediation, and prevention of pollution (Kaur et al. 2017). Additionally, nanomaterials can also be used for the improvement of membrane separation processes resulting in higher selectivity and lower cost (Gehrke et al. 2015). Nanomaterials have several advantages, such as unique size-dependent properties emerge owing to the quantum confinement effect. The specific characteristics allow the development of high-performance nanomaterials for efficient wastewater remediation (Horizon 2020). The most promising applications of nanomaterials for wastewater remediation are highlighted in Table 2.5.

Nanotechnology offers great potential in the area of water treatment and purification due to the large surface-to-volume ratios (SVR) of the nanomaterials. The preparation of novel photocatalytic membranes by implanting semiconducting nanomaterials over the conventional membranes is used for the purification and treatment process (Krishnan et al. 2008). Various approaches, such as photocatalysis, nanofiltration, and adsorption, using titanium dioxide (TiO_2), zinc oxide (ZnO), polymer membranes, ceramic membranes, carbon nanotubes, nanowire membranes, and magnetic nanoparticles (nZVI), are used to resolve problems involving treatment of wastewater (Bhattacharya et al. 2013; Andreescu et al. 2009). Novel metal/metal oxide nanoparticles, nanomembranes, and other nanomaterials are used for detection and removal of chemical and biological contaminants, including heavy metals, pharmaceutical wastes, pesticides and their intermediates, cyanide, algae,

Table 2.5 Application of nanomaterials in wastewater treatment

Nanomaterials	Properties	Applications
Metal and metal oxides	Photocatalytic	Largely used for environmental remediation
	Nontoxic	Slurry reactors
	Green chemistry based	Heavy metal, dyes, industrial effluent treatment
	Reusable	
Adsorbents	Higher surface area	Removal of heavy metals
	Higher SVR	Dyes
	Higher adsorption rates	Pesticide degradation
	Easy to modify	Removal of organic pollutants, bacteria
Membrane and processes	Reliable	Treatment of water and wastewater
	Most trusted	Purification
	Widely used	Desalination
	Automated process	All fields of water and wastewater treatment

viruses, bacteria, parasites, organics, antibiotics, etc., from wastewater (Alqadami et al. 2016; Khan et al. 2018; Adeleye et al. 2016; Naushad et al. 2015; Khin et al. 2012). Membrane processes, nano-based materials, and the combination of both offer wide possibilities for water treatment by filtration and photocatalysis at the same time (Martin 1994; Adriano et al. 2004). With the sustainability issues, the focus has been shifted toward the use of greener methods for the treatment of wastewater for environmental applications. Thus, the nanomaterials synthesized using green chemistry-based approaches used for the environmental clean-up will reduce the risk of hazardous waste generation and eliminate the risk of toxic end products.

2.2.4 *Photocatalysis or Nanocatalysis*

The inability of conventional technologies toward environment sustainability has led to the research in the field of “Advanced Oxidation Processes (AOPs)”, including the nano-based wastewater treatment technologies (Swaminathan et al. 2013). The main aim of these AOPs is the generation of highly reactive species (in situ) or generation of free radical charged particles for rapid degradation and mineralization of unmanageable organic compounds and pollutants, water pathogens, toxicants, pesticides, and disinfection by-products (Oturan and Aaron 2014; Sheldon et al. 2007).

Over the past few years, nano-based photocatalysis has shown great potential as a green chemistry-based remediation technology. Among the several green earth projects underway, nano-photocatalysis has emerged as the most promising treatment technology; it utilizes the energy of natural sunlight or artificial illumination that is available in abundance (Polshettiwar and Varma 2010). In recent years, photocatalytic processes have been successfully utilized for the elimination of these contaminants from wastewater. Photocatalytic oxidation has already proven its potential for the degradation of various compounds, such as dyes, pharmaceuticals, endocrine disrupting compounds, phenols, and pesticides, from wastewater (Oller et al. 2011). The photocatalytic processes have proven successful in the degradation and mineralization of organic bio-recalcitrant compounds and emerged as the most effective treatment technique (Sheldon 2008). The increasing public concern about several environmental pollutants has provoked the need to develop advanced treatment technologies, where advanced oxidation, i.e., photocatalysis, is gaining a lot of attention in the field of environmental remediation. There are several advantages to using nanocatalysts; they are:

(i) Nontoxic,
(ii) Low cost,
(iii) Highly efficient,
(iv) Reusable,
(v) No toxic and hazardous end product,
(vi) Efficiently work on a wide range of pollutants,
(vii) Highly reactive.

Also, the major advantage of the photocatalytic process over the existing technologies is that there is no requirement for further treatment, thus eliminating the need for secondary disposal methods. Compared to other advanced oxidation processes, especially those involving the use of oxidants, such as hydrogen peroxide and ozone, here expensive oxidizing agents are not required because atmospheric oxygen acts as the oxidant, which is the added advantage of nano photocatalysis (Kalidindi and Jagirdar 2012). As the selectivity and efficiency of nanocatalysts largely depend on the shape, size, and surface structures, synthesis of nanocatalysts having the desired physicochemical properties is a must to achieve the goal of green nanotechnology (Stasinakis 2008; Xu et al. 2012). The design and production of nanocatalysts is the basis of achieving the complete degradation of pollutants into environment-friendly end products (Anastas et al. 2001). It is among this area where nanotechnology enables green chemistry to offer a way to green nanotechnology toward sustainable remediation. It is a known fact that most of the organic and inorganic pollutants can be easily degraded by heterogeneous photocatalysis (Campelo et al. 2009). Photocatalysis is a process of degradation of pollutant by accelerating the rate of chemical reaction in the presence of a semiconductor catalyst without itself being consumed. The process principally depends on the generation of hydroxyl radicals (OH) that are capable of converting various toxicants/nonbiodegradable pollutants into nontoxic end products, such as CO_2, H_2O, and other environmentally friendly compounds (Min and Friend 2007). Nano-photocatalysis is a technology used for the removal as well as the mineralization of contaminants from the waste in order to environmentally clean-up in a sustainable manner (Mishra and Khushalani 2013). Figure 2.10 shows the photocatalytic process over the surface of a nanocatalyst.

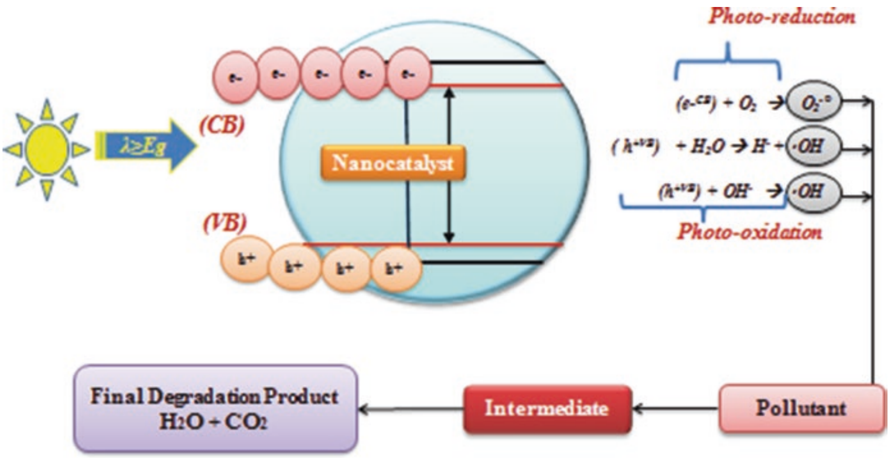


Fig. 2.10 Photocatalytic process over the surface of nanomaterial

Nano-based photocatalyst has shown potential as a low-cost, green chemistry-based, sustainable treatment technology (Ahmed et al. 2011). Most commonly used heterogeneous catalysts are semiconductors (Fenoll et al. 2011) having wide band gaps. Several types of nanomaterials, such as metal and metal oxide nanoparticles, doped nanoparticles, nanocomposites, nanotubes, and bimetallic nanoparticles, have been used for the treatment of a wide range of environmental pollutants (Berekaa 2016; Khin et al. 2012). The development of efficient semiconductor-based photocatalysts, which can work in solar, visible, and UV light, is a challenge despite substantial research in the area.

2.2.5 Water Filtration Using Nanofiltration

Membrane filtration, frequently referred to as the *"technology of choice"*, is a widely accepted and superior technology treatment of wastewater implemented by providing a barrier (physical) that effectively removes the unwanted molecules (Baker et al. 2007). For over three decades, membrane technology has been recognized worldwide for the successful separation of a wide range of contaminants from water and wastewater (Baruah et al. 2017). A membrane is a thin layer of a semipermeable material that separates substances when a driving force is applied across the membrane (Scott and Hughes 2012). Membranes provide the physical barrier that allows only certain components to pass through on the basis of their chemical and physical properties. Among all the other conventional technologies used for the treatment of water, membrane filtration emerges as the most trusted because it is very simple, highly effective, does not involve the use of chemicals and additives, is easy to scale-up, fast, and, importantly, because of its flexibility to combine with other advanced treatment technologies (Ersahin et al. 2012). The pressure driven filtration technology is classified as low pressure (MF & UF) and high pressure (NF & RO) on the basis of the molecular weight cut-off values (MWCO) of the particular membrane and trans-membrane pressure (Yangali-Quintanilla et al. 2011; Riungu et al. 2012). These four membrane filtration processes are best understood together in terms of the size of particles that can be removed from a mixture. Out of these, nanofiltration emerges as the sustainable alternative for the remediation of several contaminants.

NF is a high pressure driven technology, used to remove organic contaminants, bacteria, viruses, dairy, natural organic matter, and salts. It is also used for softening of hard water by removing multivalent and divalent ions. The pore size of the NF membrane is around 0.001 microns, typically under the range of 1–100 nm. Up to 99.9% removal of molecules in the range of 1–100 nm was achieved in the cases of different pesticides using NF membranes (Strathmann et al. 2011). NF is excellent for the removal of low molecular weight compounds, as low as 100–200 Da, and therefore selected for the removal of pesticides (Shon et al. 2005; Kim et al. 2011). Higher energy is required for NF than MF and UF. NF is the process between RO and UF, and is also referred to as loose RO. To date, NF is the only filtration technology known to remove organic contaminants and pesticides (Karimi et al. 2016).

2.2.6 Renewable Energy Generation

The major research area in this field is the design of nano-enabled solar cells utilizing the principles of green chemistry. The novel nanomaterials used for solar cells include titanium dioxide, quantum dots, cadmium telluride, and silver with a polymer that can absorb a large fraction of solar energy (Guo 2012). The cost of these nano-based solar cells will be much lower compared to those of commercially available solar cells (Wang et al. 2008). Intensive research is going on in this field to increase the efficiency of these solar cells. Other methods, such as the deposition of nano-crystals, suspended nanoparticles in quantum dots, nanowires, and the production of the highly stable laminate layer for the protection of solar cells, are also considered for sustainable product development (Musee 2011). Nanotechnology research is also happening in the field of energy storage by developing high-capacity energy storage devices for application in the area of renewable energy. Nano-based photovoltaic devices have considerable potential for high performance and cost reduction (Tennakone et al. 1995).

2.3 Limitations of Green Nanotechnology

Green nanotechnology is an emerging area, and it has its own limitations and challenges to address. According to the report of the ACS Green Chemistry Institute, the key challenges linked with green nanotechnologies are:

(i) Handling of toxicity related issues of nanomaterial
(ii) Technical and economic barriers
(iii) Regulatory policies for nanomanufacturing processes
(iv) Deployment of scale-up procedures
(v) Life cycle analysis

The above-mentioned points should be extensively considered for green and sustainable development. Green nanotechnology brings products that reduce pollutants and are eco-friendly but the major limitations are the costs and risks associated with the production of nano-based products. Though advances have been made in the development of green nanotechnology, the level of sustainability for greener applications of nanotechnology is always a concern. The products synthesized using green nanotechnologies are efficient, but the main worry lies with the upstream processing of the products (Clark 1999).

Research is under-way for the synthesis and application of greener nanoproducts, but when talking about the commercial front, there are very few products commercialized to date (Constable et al. 2002). It is a general conception that it will take a few years to fully understand the market potential of green nanotechnology.

2.4 Conclusions

Nanotechnology offers the opportunity to find the solution to global problems that significantly affect society. As the name implies, green nanotechnology has a certain green purpose. After reviewing the advances and applications of the field, the focus has been shifted to nano-based applications, as nanotechnology provides the framework to consider the application of green chemistry. Through research, it has been revealed that even after various advantages it has certain limitations and challenges to address. Green nanotechnology has the significant potential to make a contribution to addressing the green challenge along with sustainable development. The sustainable development of nanotechnology will require the incorporation of life cycle thinking to analyze the environmental impacts of the nanoproducts. Also, certain points such as possible life cycle assessment of the newly synthesized nanoproducts through nanomanufacturing before release to the commercial front must be taken seriously in accessing the contribution to the green growth. Application of the principles of green chemistry to nanotechnology helps to identify better products and processes but there is always hope for improvement.

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Chapter 3
Activated Carbon from Different Waste Materials for the Removal of Toxic Metals

Soodamani Periyasamy, Ilango Aswin Kumar, and Natrayasamy Viswanathan

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Abstract Heavy metal enters into the ecosystem from natural and anthropogenic sources. Heavy metals are toxic which leads to various types of diseases in the living organisms. Hence, the removal of heavy metals from water is very essential to minimize the toxic effects of heavy metals. This chapter explains the sources, toxic effects and treatment methods of various heavy metals. Adsorption technique seems to be the best technique for heavy metal remediation. Activated carbon (AC) is the promising adsorbents for the removal of heavy metal from water. Hence, this chapter mainly focused on AC derived from different wastes like agriculture wastes, biological wastes, fruit wastes, vegetable wastes, plastic wastes and electronic waste (e-waste) materials for heavy metal removal. Various adsorption influencing condi-

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S. Periyasamy · I. A. Kumar · N. Viswanathan (✉)
Department of Chemistry, Anna University, University College of Engineering – Dindigul,
Dindigul, Tamil Nadu, India

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tions which were optimized for heavy metal removal are discussed in detail. A possible mechanism for heavy metal removal is also given. A comparison of heavy metal adsorption capacity of AC derived from various waste materials is discussed in detail.

Keywords Activated carbon · Waste materials · Adsorption · Heavy metal removal

3.1 Introduction

Water is one of the most important resources present in the universe which is responsible for the existence of all the living organisms. For the past ten decades, water has been affected by a lot of pollutants such as heavy metals (Carolin et al. 2017; Awual et al. 2016), organic matter, domestic wastes, industrial wastes, etc. (Staples et al. 2011). Among them, heavy metals are highly dangerous because these are stable and non-biodegradable in nature which causes the serious threats and diseases to living community (Periyasamy et al. 2017). Aluminium (Al), arsenic (As), chromium (Cr), cadmium (Cd), lead (Pb), cobalt (Co), iron (Fe), copper (Cu), magnesium (Mg), molybdenum (Mo), mercury (Hg), manganese (Mn), uranium (U), nickel (Ni) and zinc (Zn) are the important toxic heavy metals which enter into the drinking water sources from various natural and man-made activities (Gopalakannan et al. 2018; Duruibe et al. 2007; Godt et al. 2006). As industrialization and civilization have grown over the last century, there has been an increase in the release of various toxic contaminants and other waste products into the water system. Although some of these metals are essential at lower concentration, the same metals cause various diseases if they exceed the tolerance limit. Hence, the World Health Organization (WHO) has assigned the tolerance limit of various toxic heavy metals in drinking water. It is also mandatory to remove the excess heavy metal ions present in water to minimize their toxic effects.

The different techniques have been reported for the removal of heavy metal such as adsorption, chemical precipitation, electrochemical precipitation, chemical oxidation, ion-exchange, membrane process, activated sludge process, electrocoagulation, electrodialysis and anaerobic process (Naushad et al. 2015; Bushra et al. 2015; Nag et al. 2017). Among them, adsorption is one of the best techniques for the remediation of heavy metal due to its unique advantages like economical, simple operation and high adsorption capacity (Aswin Kumar and Viswanathan 2018; Pandi et al. 2017).

Nowadays, the different adsorbents like polymers, inorganic materials, graphene oxide(GO), clays, activated carbon (AC), carbon nanotube (CNT), magnetic materials, covalent organic frameworks (COFs) and metal organic frameworks (MOFs) are employed for the heavy metal removal from aqueous solution (Alqadami et al. 2017). Among the adsorbents, AC and their modified materials are considered as the most effective adsorbents for the removal of various contaminants from aqueous solution because they possess large specific surface area and high micropore volume. AC is carbon fabricated from the carbonaceous sources such as coconut husk, bamboo, coir, wood, etc. In the last few decades, AC was prepared from various waste materials such as agricultural wastes, biological wastes, fruit wastes, electronic wastes, vegetable wastes and plastic wastes (Mohan et al. 2005). AC prepared from the above-mentioned waste materials has been utilized for heavy metal removal because AC materials have many attractive functional groups such as carbonyl, polyhydroxy, phenolic, acetamido, alcoholic, amido, amino, sulphydryl, etc. (Forgacs et al. 2004; Dias et al. 2007; Demirbas 2008). These functional groups are attracted by heavy metal ions via electrostatic attraction or surface metal complexation. The heavy metal adsorption mechanism has been followed by physical adsorption, chemical adsorption, complexation, diffusion and ion exchange (Babel and Kurniawan 2003; Al-Othman et al. 2011).

3.2 Sources and Toxic Effects of Heavy Metals

Heavy metals are entering into the environment by both natural and anthropogenic activities. The important natural sources of heavy metals are weathering of minerals, volcanic activity, soil erosion, ores, forest fires and bio-fertilizers (Alloway 2013). Commonly, soils have various metal minerals and ores like chalcopyrite (Cu), gold veins in rock (Au), hematite (Fe), molybdenite (Mo) and sphalerite (Zn). The anthropogenic sources of heavy metals are industrial effluents, inorganic fertilizers, sewage wastes and fossil fuels (Periyasamy et al. 2018; Luo et al. 2015). Due to the rapid industrialization and commercial life style, the anthropogenic sources of environmental pollution have increased day by day. The list of anthropogenic sources, tolerance limit and toxic effects of heavy metals is demonstrated in Table 3.1.

3.3 Heavy Metal Removal by Various Methods

Nowadays, numerous types of chemical, physical and biological methods have been utilized for heavy metal removal from water. However, they have their own advantages and disadvantages which are listed in Table 3.2 (Gunatilake 2015; Azimi et al. 2017; Malik et al. 2017).

3.4 Advantages of Heavy Metal Adsorption

Adsorption is one of the best methods for the technological decontamination of water because it is effective, economical and eco-friendly (Sharma et al. 2017). In addition, the various adsorbents prepared for adsorption process can be highly regenerated than the other methods (Aswin Kumar and Viswanathan 2018; Pandi

Table 3.1 Various sources, tolerance limit and toxic effects of heavy metals

Heavy metals	Sources	Tolerance limit	Effects on the living organisms
Chromium (Cr)	Metal finishing, mining, electroplating, tannery and leather industries	0.05 ppm	Its carcinogenic nature leads to cancer, kidney and liver damage
			It reduces the growth of plants, grain weight and weight of vegetables
Lead (Pb)	Lead acid battery, paints, electronics, metallurgical, ceramics and pesticide industries	0.05 ppm	It causes harmful effects on human brain and nervous systems. It damages the circulatory system and kidney function. It leads to high blood pressure
Mercury (Hg)	Electronics, electrical manufacturing and coal combustion industries	0.001 ppm	It causes harmful effects on the human nervous system, digestive system, kidney function and circulatory function
Copper (Cu)	Mining, electroplating, smelting and refining industries	0.01 ppm	It affects the human blood coagulation. It leads to melena, hypertension, Wilson diseases, gastrointestinal distress and insomnia
Arsenic (As)	Pesticide/insecticide, smelting operations, thermal power plants and metallurgical industries	25 ppb	It leads to skin cancer, visceral cancer, kidney failure, bladder damage, abdominal pain and visceral cancer
			It also decreases red and white blood cell production in the human body
Cadmium (Cd)	Metal plating, pigments, paints, plastic production, fertilizer and pesticide industries	0.01 ppm	It is carcinogenic which leads to itai-itai disease, kidney damage and renal disorder
Iron (Fe)	Metallurgical, steel manufacturing, pharmacy production, heavy machinery, food and medicine industries	1.0 ppm	The overload of iron content causes mutation in the gene. It also causes stomach problems, nausea and vomiting
Zinc (Zn)	Pyrometallurgical, electroplating, cosmetics, pharmaceuticals, plastics, inks, textiles, batteries, soaps and electrical equipment industries	0.5 ppm	It leads to hypertension, lethargy, neurotic effects and edema of lungs. Excess of zinc in drinking water affects the internal organs in living organisms
Nickel (Ni)	Smelting operations, thermal power plants, alloys and battery industries	2 μg/L	It causes lung embolism, asthma and liver and kidney damage with chronic bronchitis

Table 3.2 Advantages and disadvantages of various heavy metal removal techniques

Heavy metal removal methods	Advantages	Disadvantages
Electrochemical treatment	Highly selective, no sludge production and nonhazardous	High cost of electricity
Oxidation	Rapid removal capacity for toxic metal removal	Costly and formation of secondary by-products
Precipitation	Relatively simple, non-metal selective and inexpensive	Secondary pollution formation, large production of sludge, poor settling time and slow metal precipitation
Coagulation/ flocculation	Economical and simple technology	High sludge production and formation of large particles
Ion exchange	Metal selective, fast rate and high regeneration efficiency	High maintenance cost
Membrane process	Easy operation, efficient loading capacities and gets high-quality effluents	High cost, low flow rate and possesses the limited screen size
Adsorption	High efficiency, non-toxic, environmentally compatible and easily operated	Removal capacity depends upon the nature of adsorbents and highly pH-dependent
Ozonation	Reaction by-products are less harmful, short reaction time and gets high quality of water	Equipment malfunction, some ozone produce by-products, higher initial cost and regeneration is not possible
Aerobic process	Fewer operational problems, less daily maintenance and lower BOD produced	Higher energy requirements and high sludge productions
Filtration	Low cost and easy to operate	Not suitable for the removal of all heavy metals, very low flow rate and non-selective

et al. 2017; Gopalakannan and Viswanathan 2015). It is a process which is strong enough to realize the water reuse requirement and high run-off standards in the industries. Adsorption of heavy metal is a mass transfer process in which the metal ion is transferred to the surface of the adsorbent and becomes bounded by the physical or chemical interactions (Kousalya et al. 2010). In addition, the bonding nature in the adsorption of heavy metals are shown in a clear manner. The physical and chemical adsorption process can occur in the environment at low temperature with appropriate pH condition.

Many adsorbent materials such as inorganic, organic, polymeric, MOF, COF, clay, AC, biomass and waste carbon source materials have been utilized for heavy metal removal. Among the adsorbents examined for heavy metal removal, AC from various waste materials due to be low cost and also a very efficient material. This chapter is focused on the development of AC from the inexpensive waste materials and its unique properties like high affinity, selectivity and high adsorption capacity towards heavy metal removal were discussed. The potential of various agricultural and industrial waste materials has received the most attention for heavy metal removal from the water/wastewater.

3.5 Origin of Activated Carbon

Initially, AC has been used by Egyptians as adsorbent for the medicinal purposes and as purifying agent in 1500 BC. Sweden Chemist, Karl Wilhelm Scheele, has utilized the charcoal for the adsorption of gases in 1773. A few years later, AC was utilized in the sugar industry as a decolourizing agent. In the twentieth century, the first AC plant was developed in Germany, and it was utilized as sugar-purifying/decolourization agent. In 1900, the production of AC from various plants was applied as the decolourization agent for both pharmaceutical and food products. Nowadays, AC plays a vital role in various applications such as water purification, sewage treatment, medicine, air purification, fuel storage, metal extraction, hydrogen storage and decaffeination.

3.6 Preparation of Activated Carbon-Supported Materials

AC has been broadly applied in air purification, energy storage and water treatment especially for the removal of toxic metal ions owing to its abundant pore textural properties like large specific surface area, average pore width, micropore volume and assets of the exterior oxygen containing active functional groups (Ayranci and Duman 2009). AC was synthesized from various carbonaceous materials such as agriculture wastes, biological wastes, fruit wastes, vegetable wastes, plastic wastes, e-wastes, etc., by the carbonization process followed by physical or chemical activation (Abioye and Ani 2015; Skodras et al. 2007; Shehzad et al. 2015; Kumar et al. 2018).

3.6.1 Physical Activation

Physical activation is one of the pyrolysis processes which mainly occurred at high temperature. This process involves two steps, namely, carbonization of carbonaceous materials in an inert atmosphere and the activation of the resulting materials in the presence of carbon gasification reactants such as carbon dioxide, stream or air. Physical activation process is involved between the carbon atom and the oxidizing gas. Fatima Salgado et al. have synthesized AC from babassu endocarpunder (Brazilian palm) using physical activation method. They also reported the efficiency of AC product as 79.09, 80.94 and 83.72% at 700, 750 and 800 °C, respectively. The BET surface area of babassu endocarpunder AC was found to be 543.56, 480.74 and 542.19 m^2/g at 700, 750 and 800 °C, respectively (Fatima Salgado et al. 2018).

3.6.2 Chemical Activation

Chemical activation is one of the chemical processes occurring in a single-step reaction in which the raw carbon source materials are impregnated with the suitable chemicals. In this method, the solid activation agents like alkali, alkaline earth metal containing salts and some acid/bases such as sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, potassium hydroxide and sodium hydroxide have been utilized for the production of AC (Hui et al. 2009). The temperature employed in chemical activation is lower than that of physical activation. In addition, the chemical activation process offers a higher surface area of AC (>3000 m^2/g) than physical activation. Limousy et al. have synthesized AC from the phosphoric acid-activated olive stone and successfully utilized it for amoxicillin removal from aqueous solution. The obtained specific BET surface area and pore volume of AC by olive stone were found to be 1174 m^2/g and 0.46 cm^3/g, respectively (Limousy et al. 2017). Tran et al. have prepared an efficient AC from the golden shower tree flower via chemical activation which provides the high surface area of 1413 m^2/g (Tran et al. 2017).

3.7 Activated Carbon from Different Waste Materials for Toxic Metal Removal

AC is the promising adsorbent for the removal of heavy metals from water. The AC prepared from the waste materials seems to be cost-effective and possess high removal capacity. The sources of AC-based waste materials can be divided into two categories: natural and man-made wastes. The natural wastes are created by the usage of natural materials such as agriculture products, vegetables, fruits, woods and seeds. The man-made wastes created by human activities include industrial, municipal, plastic and e-wastes. These waste materials can be utilized for the synthesis of AC which can be applied in various wastewater treatments especially the removal of heavy metal. In addition, the large surface area and the high micro-mesoporous structure of AC can be prepared by either physical or chemical activation of AC which helps to enhance the heavy metal adsorption capacity. The derived AC from different sources of waste materials developed for the removal of various heavy metals from water is discussed as follows.

3.7.1 Activated Carbon from Agricultural Wastes

Agricultural waste is unsalable or unwanted materials produced entirely from the results of various agricultural operations which directly related to the growing of crops. Agricultural waste materials could be used as the resource materials in many fields such as engineering, medical, wastewater treatment, etc. A lot of agricultural wastes such as rice husk, tamarind seeds, corn cobs, groundnut shell, etc. have been produced day by day in various agricultural processes. These waste materials are biodegradable and can be easily converted into AC which is often applied for heavy metal removal from water.

Shrestha et al. have developed the agricultural waste product seed-generated AC, namely, Lapsi (*Choerospondias axillaris*), which is available in the subcontinent of India. The major purpose of their work was to improve the easiest chemical method which is adopted for the chemical activation of Lapsi seed and carbonization for Pb(II) and Ni(II) removal. The higher adsorption capacity of AC which derived from Lapsi seed occurred by the use of chemical carbonization process. The experimentally observed adsorption capacities of Pb(II) and Ni(II) were found to be 424 and 70 mg/g, respectively (Shrestha et al. 2013).

Kadirvelu et al. have prepared AC from the numerous solid wastes obtained from agricultural such as sago waste, coconut tree sawdust, silk cotton hull and maize cob for Ni(II) adsorption from aqueous solution. The adsorption of Ni(II) requires a very diminutive time period and gives the quantitative removal as well. The experimental result of AC obtained from the agriculture waste materials was effective in Ni(II) removal from water. Since all the solid wastes applied in this exploration are locally available and abundant in nature, this ensuing AC was projected as an inexpensive material for the wastewater treatment. These biowaste materials were collected from the agricultural processing industries in and around Coimbatore, Tamilnadu, India. These materials were converted into AC using concentrated H_2SO_4. The removal of Ni(II) was carried out in batch scale using coconut tree sawdust, sago waste, silk cotton hull and maize cob which was found to be 81, 100, 58 and 100%, respectively (Kadirvelu et al. 2003).

The effluent treatment at various water sources is necessary for any industry to overcome the problems of adverse public health, economic and environmental impacts caused by excess Cd(II) in water. The pretreatment of Cd(II) effluent up to the safe limit can only resist the hazardous Cd(II) to reach the water bodies and natural environment. Nag et al. have developed the naturally obtainable agriculture waste materials, viz. rubber plants, mango leaves and jackfruit leaves, which have been utilized for the preparation towards the toxic Cd(II) removal from aqueous medium. The surface characteristic properties like porous morphology and high surface area facilitate the adsorption process. The adsorption of Cd(II) was controlled by intraparticle diffusion, mass transport and chemical adsorption process. Jackfruit leaf showed the best adsorption performance of 20.37 mg/g for Cd(II) removal. In addition, the prepared AC from jackfruit leaf performed satisfactorily when tested for the collected industrial wastewater as well (Nag et al. 2018). Recently, microwave heating method has been utilized for AC synthesis toward the removal of heavy metal by low-cost vegetable wastes. The conservative heating process was adopted frequently for AC synthesis which involves the fabrication of electrical energy heater and involves elevated energy use and long-time processes; thereby, microwave technology was improved for the preparation of AC (Wang et al. 2012a, b).

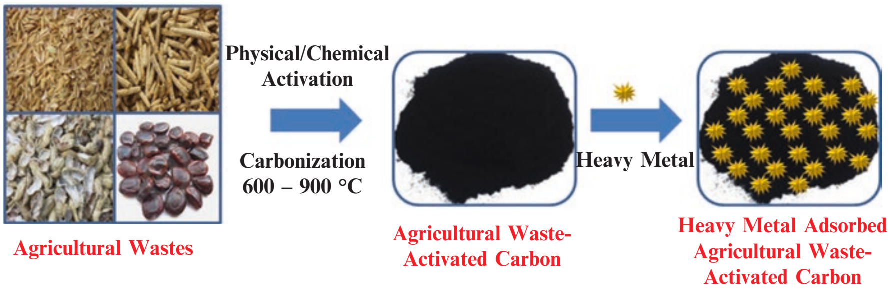

Fig. 3.1 Synthesis of activated carbon from agricultural waste materials for heavy metal removal

In addition, olive stone (OS) waste residue is a raw material used for AC fabrication which can be considered as the better material because it is abundant and quite cheap. The International Olive Council has reported that the annual invention of olive oil worldwide in the year 2012 was almost more than 3 million tons, and approximately 15 million tons of olive cakes are gained (Vossen 2007). Taking these into consideration, Alslaibi et al. have developed the microwave technology for the synthesis of olive stone (OS)-generated AC (OSAC) towards Cd(II) removal (Alslaibi et al. 2013). The removal percentage of 95.32% was observed for Cd(II) adsorption using OSAC, and also the microwave-applied OSAC can be applied for the efficient Cd(II) adsorption from wastewater at field condition. The carbonization process of carbon-containing raw materials is the requirement step for the easiest preparation of AC. However, the carbon porosities are not efficiently improved for the need of practical applications. So, carbonization followed by thermal activation has applied for the preparation of AC in which the process occurred under the flow of CO_2 or steam.

Chand et al. have synthesized the porous AC materials from the agro-waste barley straw (BS) and wheat straw (WS) by applying the carbonization process, and the prepared AC has been utilized for Cr(VI) removal from aqueous solution (Chand et al. 2009). The Cr(VI) adsorptive removal investigation occurred at a carbonization temperature of 800 °C at pH 2. The carbonized barley straw (CBS) and carbonized wheat straw (CWS) materials obtained from the agro-wastes were found to have the higher Cr(VI) adsorption capacities of 44.89 and 43.75 mg/g respectively. In addition, it requires the equilibrium time of 1 h for Cr(VI) removal. Chun-Shui et al. have developed an agricultural by-product called peanut hull which is most abundant in nature and utilized for Cu(II) removal from aqueous solution (Chun-Shui et al. 2009) (Fig. 3.1).

The Cu(II) adsorption was pH-dependent and maximum at pH 5.5 at 2 h of equilibrium time. The activation energy (Ea) of Cu(II) adsorption was found to be 17.02 kJ/mol which shows that peanut hull bioadsorbent has been activated with chemical method, and the adsorption capacity for Cu(II) was observed as 21.25 mg/g at 30 °C. Mohan et al. have focused on the decontamination of Cr(III) from drinking water using low-cost AC which was synthesized from the coconut shell fibres. The coconut shells that are the current grim disposal trouble in the environment were collected from Lucknow, India. In this study, AC was synthesized by treating 2 g of coconut shell fibres with 20 mL of concentrated sulfuric acid, and this mixture was kept in an oven at 150–165 °C for 24 h. Finally, the carbonized material was washed well with double distilled water to remove the excess acid and dried at 105–110 °C for 24 h. The dried coconut shell fibres were get in through the removal of Cr(III) from water, and the adsorption capacity was observed as 39.56 mg/g (Mohan et al. 2006).

Hegazi has focused on utilizing the possible sources of agro-based inexpensive rice husk adsorbent for the feasible removal of heavy metals from water. He focused on contributing less expensive adsorbents for various agricultural waste products, which are also pollution sources. In this study, Fe(II), Pb(II), Cd(II), Cu(II) and Ni(II) ion solutions of 20, 30, 40, 50 and 60 mg/L were taken for adsorption studies. Fe, Pb, Cd, Cu and Ni removal using rice husk has the percentage removal efficiency of 99.25, 87.17, 67.91, 98.18 and 96.95%, respectively (Hegazi 2013).

3.7.2 Activated Carbon from Biological Wastes

The biological waste materials that exist in nature are capable of self-replication and may produce the effects upon biological organisms. The important biological waste materials include buffing dust, bovine skin obtained from leather industries, etc., which may cause itself a serious problem until it gets disposed or reused. Hence, the preparation of AC from these biological waste materials has been taken into account in which it is applied in the environmental remediation (Gil et al. 2014) (Fig. 3.2).

Lopez-Anton et al. have studied AC of biowastes obtained from the vegetable tanning process and demonstrated for the adsorption of Hg(II) capture in oxy-combustion process. The high proportion of Hg oxidizes to Hg(II) under AC is very important to consider that the cost-effective mode, in order to diminish Hg(II) emissions during coal combustion process and 60% of Hg(II) removal was observed (Lopez-Anton et al. 2015).

Fig. 3.2 Synthesis of activated carbon from biological waste materials for heavy metal removal

3.7.3 Activated Carbon from Fruit Wastes

Fruit wastes occur when sorting and selecting are done during the fruit production processes. The development of fruits may produce two types of waste as the solid waste of peel/skin, seeds, stones, etc. and the liquid waste of juice and its wash waters. The various solid fruit wastes like orange peels, banana peels, grape seeds, pomegranate peels, palm shells, medlar seeds, etc. are utilized for the preparation of AC for pollutant removal from water (Guo and Lua 2000; Issabayeva et al. 2006). In recent years, the attention to palm shell has improved as it can be an exceptional source for the preparation of high-quality AC. A study also showed that the palm shell AC has elevated adsorption capacity to capturing Pb(II) ion compared with other types of AC (Daud and Ali 2004). Issabayeva et al. have focused on the preparation of column packed palm shell assisted AC for the continuous adsorption of Pb(II), and the adsorption capacities are found to be 90.2 mg/g at pH 5 (Issabayeva et al. 2008). Likewise, Choong et al. have synthesized the magnesium silicate-impregnated palm shell waste powdered AC for the removal of Pb(II) from water, and the adsorption capacity of 419.9 mg/g was observed (Choong et al. 2018).

Awwad et al. have prepared AC derived from date seeds (DS) via physical and chemical activation. The raw DS material was activated under pure steam with N_2 gas, and the chemically activated DS was prepared by the addition of 10% calcium acetate. The prepared AC was studied for the removal of assorted metal ions like Co(II), Fe(III), Pb(II) and Zn(II) from water, and almost 95% removal percentage of all the toxic metals was observed. The high removal of the toxic metal ions can be explained through the chemical or physical activation as follows: (i) AC by steam pyrolysis process and (ii) AC by single-step steam pyrolysis at 700 °C with N_2 activation. The adsorption capacities of Co(II), Fe(III), Pb(II) and Zn(II) were found to be 1317, 1555, 1261 and 1594 mg/g, respectively (Awwad et al. 2013) (Fig. 3.3).

An additional solid waste with a large potential for the synthesis of AC is medlar seed waste. Medlar (*Mespilus germanica*) is an apple-shaped fruit with a reddish-tinged colour which carries different sizes (diameter, 1.5–3 cm; weight, 10–80 g). Medlar has been used in the form of jam, marmalade and jellies which has been commercially observed by food industries. In addition, it has been applied for the treatment of diuretic, bladder and kidney stones (Gruz et al. 2011). Solgi et al. have

Fig. 3.3 Synthesis of activated carbon from fruit waste materials for heavy metal removal

focused on the characterization of novel AC from medlar seed for Cr(VI) removal. The obtained medlar seed (*Mespilus germanica*) was chemically activated using KOH, and the carbonization process occurred at different temperatures of 450, 550, 650 and 750 °C. The maximum adsorption capacity of Cr(VI) on AC obtained from medlar seed was observed as 200 mg/g (Solgi et al. 2017). Likewise, Silva et al. have prepared AC from *Malpighia emarginata* grinded seeds for the removal of Cd(II) and Cu(II) in aqueous solution. The adsorption capacities of *Malpighia emarginata* seeds were found to be 103 and 98 mg/g for Cd(II) and Cu(II), respectively (Silva et al. 2017).

Gupta and Gogate have investigated the application of ultrasound technique on the activated watermelon shell-based bioadsorbent for the adsorption of Cu(II) from aqueous solution. The observed watermelon shells were let to dry under the sunlight for 48 h. Further, the shells were heated in the hot air oven at 120 °C overnight. Then, the dried watermelon shells were then powdered and then sieved in order to get the uniform particles of size, and the sieved watermelon shell powder was then mixed with stock 0.1 M citric acid solution. Considering the significant effects of the sonochemical processes, the effect of ultrasonic power indulgence on the adsorption rate has also been investigated. In order to attain the intensified adsorption by the combination of ultrasound with AC has been studied. The result shows that the watermelon treated with calcium hydroxide and the watermelon treated with citric acid adsorbents were utilized for the removal of Cu(II) from water, and the adsorption capacities were found to be 31.25 and 27.02 mg/g, respectively (Gupta and Gogate 2015).

3.7.4 Activated Carbon from Vegetable Wastes

These waste materials mainly comprised of the various vegetable matters. These vegetable waste materials can be easily decomposed by microorganisms. Nowadays, a lot of vegetable wastes such as soybean hulls, pumpkin stem waste, putrescible vegetables, etc. have been utilized for the preparation of AC towards toxic metal removal from water. Generally, they are burnt in the air to attain the function of the rapid removal of soil and water pollution in the environment (Nahil and Williams 2010).

At present, the different types of vegetable waste materials have been utilized for the adsorption of various toxic metal ions from water. One of them is carrot residue (CR) which is readily available in nature, and their use as adsorbents seems appropriate. Nasernejad et al. have developed the comparison studies for the adsorption modelling of heavy metals like Cr(III), Cu(II) and Zn(II) from wastewater by CR. CR is composed of lignin and cellulose with the removal capacity to bind metal cations due to the available functional groups like carboxylic and phenolic groups (Dhiman et al. 2017). The attained CR was dried overnight at 60 °C, and the obtained AC was chemically modified for the use of adsorption process. The adsorption capacities of AC obtained from CR residue were found to be 32.74, 45.09 and 29.61 mg/g for Cu(II), Cr(III) and Zn(II), respectively (Nasernejad et al. 2005). The use of different chemically modified cassava waste biomass for the enhancement of the adsorption of metal ions such as Cd(II), Cu(II) and Zn(II) from aqueous solution was reported by Abia et al. Cassava as *garri*, *foofoo* and starch is considered as a fast food in Nigeria which generates the large amounts of wastes and which has been often creating the environmental trouble in the region. The cassava waste biomass was chemically modified by thiolation and applied for the adsorption studies, and it possesses the adsorption capacities of 0.94, 1.01 and 0.95 mg/g for Cd(II), Cu(II) and Zn(II) compared to the unmodified cassava waste biomass which possesses slightly lower adsorption capacities of 0.87, 0.89 and 0.92 mg/g for Cd (II), Cu (II) and Zn (II), respectively (Abia et al. 2003).

Marshall et al. have proposed the enhanced metal adsorption by soybean hulls modified with citric acid for Cu(II) removal. Soybean hulls have been modified with citric acid (CA) at 120 °C for 90 min. The result shows that CA-modified hulls possess the adsorption capacities of 2.44 mmole/g for Cu(II) adsorption which was much greater than the unmodified soybean hulls which hold the removal capacities of 0.39 mmole/g (Marshall et al. 1999). Similarly, Horsfall and Abia have developed cassava waste biomass (Manihot sculenta Cranz) for the adsorption of two divalent ions Cd(II) and Zn(II) under untreated and differentially acid-treated conditions. The Cd(II) and Zn(II) adsorption capacities were found to be 86.68 and 55.82 mg/g for untreated and 647.48 and 559.74 mg/g for acid-treated biomass, respectively (Horsfall and Abia 2003) (Fig. 3.4).

3.7.5 Activated Carbon from Plastic Wastes

Plastic waste is a waste that refers to a wide range of synthetic organic amorphous solid materials which derived from natural gas and oil. The numerous plastic waste materials such as polyethylene terephthalate bottles, rubber tyres, polystyrene tyres, etc. are converted into AC and utilized for heavy metal removal from water. The precursor, namely, polyethylene terephthalate (PET), from bottle waste has been utilized for the synthesis of AC by chemical activation with potassium hydroxide (KOH) and physical activation with steam under limited heating levels and

Fig. 3.4 Synthesis of activated carbon from vegetable waste materials for heavy metal removal

Fig. 3.5 Synthesis of activated carbon from plastic waste materials for heavy metal removal

atmospheric condition. Wang et al. have reported on the preparation of chelating fibres with waste PET fibres for the various heavy metal ion removal from water (Wang et al. 2012a, b). To extend the application of PET in the adsorption system, Mendoza-Carrasco et al. have synthesized the high-quality AC from PET bottle waste for Fe(III) removal, and PET-derived AC holds the adsorption capacity of 659 mg/g (Mendoza-Carrasco et al. 2016) (Fig. 3.5).

3.7.6 Activated Carbon from Electronic Wastes (e-Wastes)

Electronic waste or e-waste refers to discarded electronic or electrical devices. The sources of e-wastes are mobile phones, discarded computers, entertainment device electronics, office electronic equipment, refrigerators and television sets which are destined for resale, reuse, recycling, salvage or disposal, etc. A low-cost AC material derived from many e-wastes such as printed circuit boards and disposal of printed track boards has been utilized for heavy metal removal from water. In electronic industries, e-waste materials have become the most important problems raised by the public in the past few years. With more common information of the various electronic equipments, the product life has been reduced, and more outmoded products are becoming superseded, thus lifting the serious environmental trouble when disposed into the water system (Xiang et al. 2006).

The printed circuit boards (PCBs) are centre constituents in the electronic products. The most eco-friendly technologies presently utilized for PCB recycling split the PCBs into a metallic and non-metallic powder (Wong et al. 2007). Xu et al. have focused on the idea of recycling the e-waste material in order to develop the AC for the treatment of the various heavy metals especially in Cd(II)-mixed wastewater. The maximum uptake capacity of the newly derived PCB material for Cd(II) has reached 2.1 mmole/g. This value shows that this material can effectively remove Cd(II) from the effluents (Xu et al. 2014) (Fig. 3.6).

The huge disposal of printed track boards (PTBs) worldwide leads to the ecological threats for adequate solution. Mainly, the modified non-metallic fraction of this waste develops nano-AC material with the suitable functionalization. Hadi et al. have developed AC derived from PCB which acts as the attractive adsorbent material for capturing the toxic metals from effluents especially the removal of Cu(II),

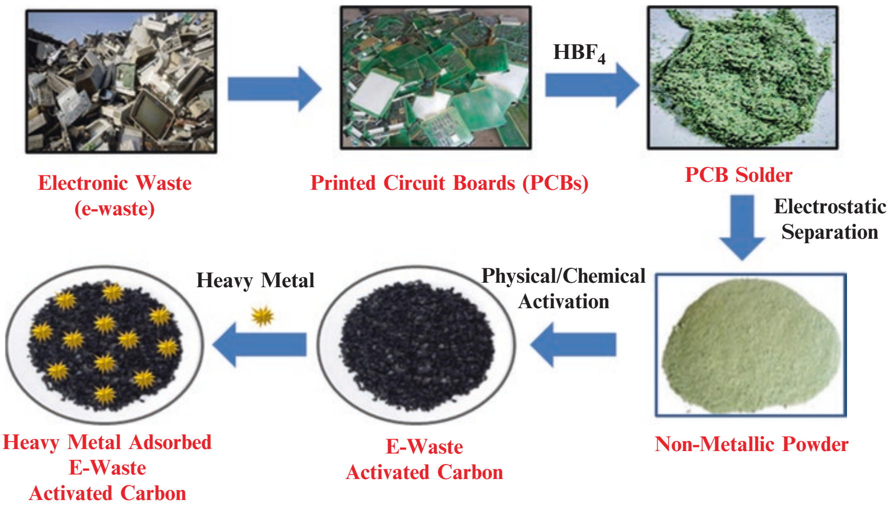

Fig. 3.6 Synthesis of activated carbon from electronic waste materials for heavy metal removal

Pb(II) and Zn(II) in single-component solutions, and the adsorption capacities of 92.94, 112.17 and 64.10 mg/g were observed, respectively. Furthermore, the limited selectivity was attained in the binary solution of Pb(II) and Cu(II), whereas a complete selectivity in the Zn(II)-containing binary solution was demonstrated using AC generated from PTB (Hadi et al. 2014).

3.8 Development of Functionalized Activated Carbon for Heavy Metal Removal

Functionalization is the progress of adding fresh functions, properties or capabilities to the adsorbent by changing the surface nature of the adsorbents. It also plays a vital role in various fields such as textile engineering, material chemistry, biological engineering and nanotechnology. To enhance the adsorption capacities of AC towards heavy metal, the functionalization of various active functional groups has been introduced on AC. The functional groups such as -COOH, -OH, amine, thiol, etc., have been focused on the functionalization of AC derived from waste materials (Yao et al. 2016). The incorporation of these functional groups possibly enhances the number of active sites on AC surface which increases the interaction of toxic pollutants, thereby enhancing the adsorptive capacity. Recently, Lalhmunsiama et al. have focused on the simultaneous removal of Hg(II) using succinic anhydride-functionalized AC derived from areca nut waste, and the removal capacity was found to be 11.23 mg/g (Lalhmunsiama et al. 2017). The comparison of adsorption capacities of AC derived from various waste materials for the removal of heavy metal are shown in Table 3.3. The AC derived from various waste materials possesses the appreciable heavy metal removal capacity (Fig. 3.7).

Table 3.3 Evaluation of adsorption capacities of AC derived from different waste materials for the removal of toxic heavy metal ions

S. no.	Sources of activated carbon materials	Heavy metal	Adsorption capacity (mg/g)	References
1	Lapsi seed	Pb(II)	424	Shrestha et al. (2013)
2	Lapsi seed	Ni(II)	70	Shrestha et al. (2013)
3	Sawdust	Zn(II)	14.10	Naiya et al. (2009)
4	Sawdust	Cd(II)	26.73	Naiya et al. (2009)
5	Neem bark	Zn(II)	13.29	Naiya et al. (2009)
6	Neem bark	Cd(II)	25.57	Naiya et al. (2009)
7	Jackfruit leaf	Cd(II)	20.37	Nag et al. (2018)
8	Olive stone	Cd(II)	11.72	Alslaibi et al. (2013)
9	Wheat straw	Cr(VI)	43.75	Chand et al. (2009)
10	Barley straw	Cr(VI)	44.89	Chand et al. (2009)
11	Peanut hull	Cu(II)	21.25	Chun-Shui et al. (2009)
12	Coconut shell	Cr(III)	39.56	Mohan et al. (2006)
13	Rice husk	Ni(II)	0.089	Hegazi (2013)
14	Rice husk	Pb(II)	0.91	Hegazi (2013)
15	Rice husk	Fe(II)	3.7	Hegazi (2013)
16	Rice husk	Cu(II)	4.10	Hegazi (2013)
17	Palm shell	Pb(II)	90.20	Issabayeva et al. (2008)
18	Date pits	Co(II)	1317.52	Awwad et al. (2013)
19	Date pits	Fe(III)	1555.20	Awwad et al. (2013)
20	Date pits	Pb(II)	1261.03	Awwad et al. (2013)
21	Date pits	Zn(II)	1594.00	Awwad et al. (2013)
22	*Malpighia emarginata*	Cd(II)	103	Silva et al. (2017)
23	*Malpighia emarginata*	Cu(II)	98	Silva et al. (2017)
24	Watermelon shell	Cu(II)	31.25	Gupta and Gogate (2015)
25	Polyethylene terephthalate	Cu(II)	659	Wang et al. (2012a, b)
26	Printed circuit boards	Cd(II)	10.8	Xu et al. (2014)
27	Medlar seed	Cr(VI)	200	Solgi et al. (2017)
28	Printed track boards	Cu(II)	92.94	Hadi et al. (2014)
29	Printed track boards	Pb(II)	112.17	Hadi et al. (2014)
30	Printed track boards	Zn(II)	64.10	Hadi et al. (2014)
31	Bagasse fly ash	Cd(II)	1.24	Tan et al. (2008)
32	Plum stone	Cu(II)	48.31	Parlayici and Pehlivan (2017)
33	Plum stone	Pb(II)	80.65	Parlayici and Pehlivan (2017)
34	Sawdust	Ni(II)	10.47	Rehman et al. (2006)
35	*Imperata cylindrica* leaf powder	Pb(II)	13.50	Hanafiah et al. (2006)
36	Carrot residues	Cr(II)	45.09	Nasernejad et al. (2005)

(continued)

Table 3.3 (continued)

S. no.	Sources of activated carbon materials	Heavy metal	Adsorption capacity (mg/g)	References
37	Sugarcane bagasse	Cu(II)	114	Junior et al. (2006)
38	Corn carbs	Cd(II)	19.3	Leyva-Ramos et al. (2005)
39	Tea waste	Cr(VI)	21.23	Wen et al. (2017)
40	Tea waste	As(V)	38.03	Wen et al. (2017)
41	Iron (III)-impregnated sugarcane bagasse	Cr(VI)	12.22	Zhu et al. (2012)
42	Peanut hull pellets	Cd(II)	6.0	Brown et al. (2000)
43	Peanut hull pellets	Cu(II)	10.0	Brown et al. (2000)
44	Peanut hull pellets	Pb(II)	30.0	Brown et al. (2000)
45	Areca nut waste	Hg(II)	11.23	Lalhmunsiama et al. (2017)
46	Waste mixture	Co(II)	83.6	Kenawy et al. (2017)

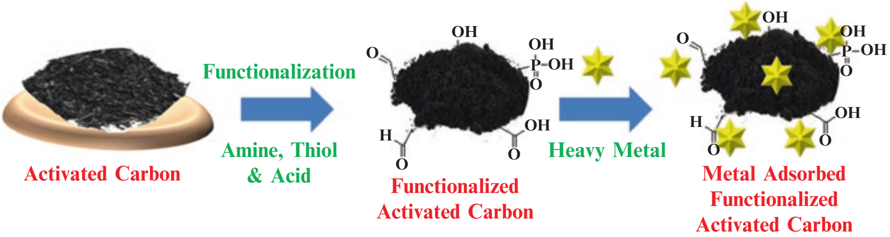

Fig. 3.7 Synthesis of functionalized activated carbon for heavy metal removal

3.9 Conclusions

This chapter discussed the activated carbon obtained from the different natural waste materials for the assorted toxic metal removal from drinking/wastewater:

- A wide range of AC derived from various waste materials like vegetable, agricultural, fruit, electronic, plastic and biological wastes for heavy metal removal is presented in detail.
- AC derived from waste materials possesses advantages like inexpensiveness, high microporosity, local availability and high surface area and selectivity towards heavy metal removal.
- A comparison results in the adsorption capacity of AC derived from various waste materials was given in detail.
- The development of AC is frequently reported by worldwide researchers. However, to control the influence of multisteps in the synthesis of AC for the adsorption studies should be focused in the near future.
- Fabrication, optimization and application of AC which derived from the various waste materials are needed to concentrate at the industrial scale.

- The significant features such as the preparation techniques, the modification of the surface properties, and the regeneration studies of AC should be improved in order to make AC material as a cost-effective one.
- AC should be mixed with suitable binding materials which help to convert into usable shapes like membranes, beads, etc., for developing the heavy metal removal technology.

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Chapter 4
Bioremediation of Toxic Heavy Metals Using Marine Algae Biomass

Laura Bulgariu and Dumitru Bulgariu

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Abstract Marine algae are generally considered cheap and available materials, which do not compete with agricultural crops for land or water, and are therefore included into category of renewable biological resources. Currently, the marine algae have several industrial uses linked to biofuel production and the extraction of some important active compounds, but these applications are still limited by several technological difficulties. However, the use of marine algae biomass in the biosorption processes for environmental and wastewater remediation has become increasingly important. It is well known that the heavy metal pollution has severe negative consequences for human health and negative impact on the environment. Therefore, the potential use of marine algae to remove the content of toxic heavy metals, mainly from industrial effluents which are the main sources of environmental pollution, through the development of ecological approaches, has gained a worldwide

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L. Bulgariu (✉)
Faculty of Chemical Engineering and Environmental Protection Cristofor Simionescu,
Department of Environmental Engineering and Management,
Technical University Gheorghe Asachi of Iaşi, Iaşi, Romania
e-mail: lbulg@tuiasi.ro

D. Bulgariu
Faculty of Geography and Geology, "Al. I. Cuza" University of Iasi, Iaşi, Romania

Romanian Academy, Filial of Iasi, Collective of Geography, Iaşi, Romania

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interest. In this chapter, the performances of marine algae biomass as biosorbents for the removal of toxic heavy metals from aqueous media are evaluated, and the main possible practical applications are highlighted. The experimental factors that influence the biosorption capacity of marine algae biomass, as initial solution pH, biosorbent dosage, initial heavy metal concentration, contact time and temperature, are discussed in order to highlight the importance of well-defined experimental conditions for the use of these types of biosorbents. The isotherms and kinetics modelling of the biosorption data was also considered, because the calculated parameters can lead to development of the biosorption systems of toxic heavy metals with high bioremediation potential.

Keywords Toxic heavy metals · Marine algae · Biosorption processes · Environment remediation · Wastewater treatment

4.1 Introduction

The rapid development of industrial activities is the main characteristic of the last century, which has led to an increase in the standard of living of people. Unfortunately, with the development of the industrial sector, many environmental issues have arisen. One of the most important environmental issues is the degradation of the ecosystems' quality due to the presence of hazardous and harmful pollutants, such as heavy metals (Gautam et al. 2015; Naushad 2014). Heavy metals that get to contaminate the environment come mainly from the discharge of improperly treated industrial effluents, and for this reason, industrial activities are still considered to be one of the most important sources of environmental pollution with this kind of pollutants (Wu et al. 2015; Zhang et al. 2018). The global statistics reported by UNESCO (UNESCO 2003) have shown that at the level of 2003, the distribution of water use is 8% in domestic use, 22% in industry and 70% in agriculture. Therefore, an important quantity of water is annually used in the performing of industrial activities, but most important is that a big fraction of this water can be discharged into environment as wastewater and can contribute to environmental pollution.

It is well known that due to their industrial importance, various toxic heavy metals (Pb(II), Cd(II), Hg(II), Cr(VI), etc.) are intensively used in numerous industrial processes from mining industry, plating and smelting industry, fertilizers manufacturing, chemical industry, textile industry, pigments and plastics, etc. (Ghasemi et al. 2014; Mendoza et al. 1998; Lyer et al. 2005; Qaiser et al. 2007), and because they can't be destroyed or degraded and have an accumulation tendency in natural water sources (Volesky and Holan 1995; Qaiser et al. 2007), they have been included into categories of priority environment pollutants. Therefore, the presence of heavy metals in natural water over a maximum concentration level (Aklil et al. 2004; Aydin et al. 2008) affects the human health and decreases the quality of other biological systems, and hence the heavy metals content in the discharged industrial wastewater was established by legislation (AL-Othman et al. 2011).

Based on these considerations, removing heavy metal ions from industrial wastewater is still an important issue, both from an environmental and economic point of view. In this way environmental pollution can be prevented, and the reintroduction of heavy metals (recovered from wastewater) into industrial processes ensures the premises of sustainable development (Judd 2016).

Frequently for the removal of toxic heavy metals from industrial effluents are used methods such as chemical precipitation, coagulation/flocculation, membrane filtration, electrochemical techniques, ion exchange, etc. (Abdolali et al. 2016; Syukor et al. 2016). But, most of the time, these methods are not effective for removing low concentrations of heavy metals or are very expensive due to the high operational costs, high consumption of chemical reagents, or high energy requirements, to which it is added the generation of significant amounts of secondary sludge, which should be also properly treated (Satapathy and Natarajan 2006; Wang and Chan 2009).

Unlike these, biosorption is often considered a low-cost method that offers flexibility in design and operation, can be successfully used to remove low and high concentration of various heavy metals from aqueous effluents in different experimental conditions, minimizes the chemical reagent consumption and production of secondary sludge and allows, in most cases, the recovery of retained metal ions (Davis et al. 2003; Zhao et al. 2011). All these advantages have led to the elimination of heavy metal ions from water effluents through biosorption as an economic and ecological way that respects the principles of sustainable development. However, all these advantages largely depend on the type of biomass used as biosorbent in biosorbent processes (Vijayaraghavan and Balasubramanian 2015). This is why finding materials that are available in large quantities, cheap and easy to collect, and requires only a few stages of preparation is still one of the most important aspects in designing an effective biosorption process (Gupta et al. 2015).

Marine algae meet all these conditions and are considered a promising biological resource because they are available in many regions, do not require special growth conditions, making their productivity high, require only a few simple preparation stages and have high efficiency to retain heavy metal ions from the aqueous solution (Davis et al. 2003; Hannachi et al. 2015; Vijayaraghavan and Balasubramanian 2015). In addition, since the heavy metal biosorption involves a metabolism-independent mechanism in which the metal ions from aqueous media are bound to the surface of the cellular walls (Donmez et al. 1999; Malik 2004; Kumar et al. 2007), it is preferred to use non-viable algae as biosorbents, because they are obtained easier and their cost of preparation is lower. Under these conditions, the marine algae biomass behaves like a chemical substrate where the numerous and varied functional groups are uniformly distributed on the biomass surface, and these will represent the binding sites for the heavy metal ions from aqueous solution.

The presence of cell walls surface of various negatively charged functional groups, such as hydroxyl, carboxyl, sulphydryl, sulphate and amino groups (Donmez et al. 1999; Davis et al. 2003), makes that marine algae biomass to have a high ability to uptake toxic metal ions from aqueous media. These functional groups mainly come from the constituents of marine algae (polysaccharides, proteins, lipids), and therefore their ability to remove heavy metals largely depends on their chemical composition and, ultimately, on their type.

In this chapter, the performances of marine algae biomass as biosorbents for the removal of toxic heavy metals from aqueous media are evaluated, and the main possible practical applications are highlighted. In the analysis of biosorption process efficiency, the main experimental parameters which influence the biosorption capacity of marine algae (such as initial solution pH, biosorbent dosage, initial heavy metal concentration, contact time and temperature) are discussed, as well as the isotherms and kinetics modelling of the biosorption data. All these aspects will highlight the potential of marine algae biomass to retain toxic heavy metals from aqueous media through biosorption, with applications in the environmental bioremediation.

4.2 Sources of Toxic Heavy Metals Pollution

Industrial wastewater containing significant concentrations of heavy metals are produced in large quantities from various industrial activities. This is why the discharge of industrial effluents into the environment without proper treatment remains the main source of environmental pollution with toxic heavy metals (Dixit et al. 2015; Gautam et al. 2015). Thus, electroplating, milling, conversion-coating, anodizing-cleaning, etc. generate significant quantities of wastewater containing cadmium, lead, chromium, nickel, zinc, copper, vanadium, platinum, silver and titanium (Barakat 2011). The printed circuit board manufacturing is another source of wastewater which contains significant concentration of tin, lead, copper and nickel. Inorganic paint manufacturing produces wastewater containing chromium and cadmium compounds. Beside these, other common industrial activities such as energy production or intensive livestock production and aquaculture are responsible by the generation of important quantities of wastewater in which the concentration of toxic heavy metals, such as copper, cadmium, chromium nickel lead, zinc, etc., is significant. Table 4.1 summarizes the quantities of toxic heavy metals released in the

Table 4.1 The quantities (tones) of some toxic heavy metals released into environment from different industrial sectors in 2014 (E-PRTR 2016)

Industrial sector	Cd(II)	Cu(II)	Cr total	Ni(II)	Pb(II)	Zn(II)
Mineral industry	3	115	36	18	43	326
Metal processing	2	19	278	96	33	188
Chemical industry	0.5	13	30	20	10	117
Energy	3	35	21	36	9	0.3
Pulp and paper industry	0.9	14	4	7	3	118
Livestock production and aquaculture	–	69	–	–	–	227
Other industrial activities	0.1	2	32	2	0.3	11

Table 4.2 Examples of toxic heavy metals and their consequences on human health

Heavy metal	Human health consequences (Babel and Kurniawan 2003)	Maximum concentration limit, mg/L[a]	
		NTPA 001/2005	NTPA 002/2005
Cadmium	Kidney damage, renal disorder	0.2	0.3
Copper	Liver damage, insomnia, Wilson disease	0.1	0.2
Chromium	Carcinogenic, diarrhea, headaches	1.0	1.5
Nickel	Dermatitis, nausea chronic asthma	0.5	1.0
Lead	Kidney diseases, circulatory and nervous system damage	0.2	0.5
Zinc	Depression, lethargy, neurological signs	0.5	1.0

[a] Maximum concentration limits according with Romanian regulation (NTPA 001/2005; NTPA 002/2005)

environment from different industrial sectors in 2014, according to the data available from the European Pollutant Release and Transfer Register (E-PRTR).

Heavy metals are included in the category of persistent pollutants because they remain in the environment for a long time and due to the accumulation trend and their toxic effect have serious consequences for human health. In Table 4.2 are mentioned some of the most relevant heavy metals with large industrial applications, which have negative consequences on human health.

In addition, in order to minimize exposure of human and environment to heavy metals, wastewater regulations have been established, which limit the concentration of heavy metals that may be present in the discharged industrial effluents. In Romania, the wastewater regulation has two thresholds for heavy metal concentration, one characteristic for the industrial wastewater discharged into sewerage networks (NTPA 002/2005) and other for the industrial wastewater discharged into natural water sources (NTPA 001/2005). The maximum concentration limits of the some toxic heavy metals in wastewater according with the Romanian regulation are also summarized in Table 4.2.

Therefore, in order to prevent environmental pollution and to respect the principles of sustainable development, it is necessary to remove the heavy metals from industrial wastewater, and, if this is done by a method that allows for their recovery, this activity could have also economic benefits. Biosorption has this possibility, and finding a suitable biosorbent (such as marine algae biomass) will allow the design of a suitable industrial wastewater treatment system to remove toxic heavy metals.

4.3 Preparation and Characterization of Marine Algae Biosorbents

Marine algae are widespread in many regions of the world, being found in coastal areas of the seas and oceans. From biological point of view, marine algae are included in the "plants" category and have dimensions that can range from a few

Table 4.3 The content of carbohydrates, proteins and lipids of some marine algae

Marine algae	Carbohydrates, % (w/w)	Proteins, % (w/w)	Lipids, % (w/w)	References
Green marine algae				
Ulva lactuca	59.0	17.0	3–4	Jambo et al. (2016)
Cladophora rupestris		3.4	0.6	Maehre et al. (2014)
Ulva intestinalis		11.3	1.1	Maehre et al. (2014)
Red marine algae				
Gelidium amansii	66.0	20.0	0.2	Jambo et al. (2016)
Gracilaria verrucosa	60.8	9.9	0.8	Meinita et al. (2017)
Palmaria palmata	39.4	22.9	3.3	Kostas et al. (2016)
Chondrus crispus	21.8	19.9	0.5	Kostas et al. (2016)
Brown marine algae				
Fucus serratus	26.4	9.6	2.8	Kostas et al. (2016)
Laminaria digitata	21.7	26.8	1.9	Kostas et al. (2016)
Laminaria japonica	51.0	8.0	1.0	Jambo et al. (2016)
Undaria pinnatifida	43.0	24.0	3–4	Jambo et al. (2016)

micrometers (microscopic unicellular algae) to a few tens of meters (macroscopic multicellular algae).

Mostly, seaweeds are classified according to the colour of the pigments in their composition (Davis et al. 2003; Guiry 2012). The mixture of pigments in their chloroplasts lends characteristic colours, and thus the marine algae can be divided in three categories:

- Green algae – Chlorophyta division
- Red algae – Rhodophyta division
- Brown algae – Phaeophyta division

In addition to colour pigments, marine algae also have, in their composition, carbohydrates, proteins and lipids, whose types and concentrations differ from one category to another. Table 4.3 shows the content of each of these component classes for some marine algae. Thus, the cell walls of green algae mainly contain cellulose and proteins bonded to polysaccharides (Romera et al. 2007; Wang et al. 2009). The red algae have in their composition cellulose (as structural support polysaccharide), agar and carraghenates (Romera et al. 2006; Romera et al. 2007). The brown algae generally contain cellulose (i.e., the structural support), alginic acid and sulphated polysaccharides (Lodeiro et al. 2005; Romera et al. 2007).

Differences in the composition of marine algae determine a different structure of cell walls, which is one of the main factors influencing the ability of marine algae to uptake heavy metal ions from aqueous media. This is because the constituents of marine algae cell walls have different functional groups (such as hydroxyl, carboxyl, carbonyl, amino, sulphate, etc.) that can interact with heavy metal ions from aqueous media (often trough ion exchange) and thus will play an important role in the biosorption processes.

The nature of the functional groups in the marine algae structure can be easily identified from the FTIR spectra recorded for dry biomass. The absorption bands from FTIR spectra can be assigned to various functional groups in function of the maximum absorption wave numbers and using the correlation tables. Figure 4.1 shows the FTIR spectrum of *Ulva lactuca* marine algae and illustrates the main functional groups identified in this spectrum.

Such functional groups have been identified in the FTIR spectra of all categories of marine algae (Donmez et al. 1999; Davis et al. 2003; Lesmana et al. 2009; Romera et al. 2007; Wang et al. 2009) and have been considered to be the binding sites for the heavy metal ions from aqueous solution. But, in the structure of marine algae cell walls, these functional groups are not in free forms. The high concentration of Ca^{2+}, Mg^{2+}, K^+ and Na^+, ions in seawater (which is the natural growth medium), makes that these ions bound to these functional groups. The high content of alkaline and alkaline earth metal ions in the composition of marine algae (Table 4.4) is another advantage from biosorption perspective, because these cations will be easily replaced by the heavy metal ions through a simple ion-exchange process.

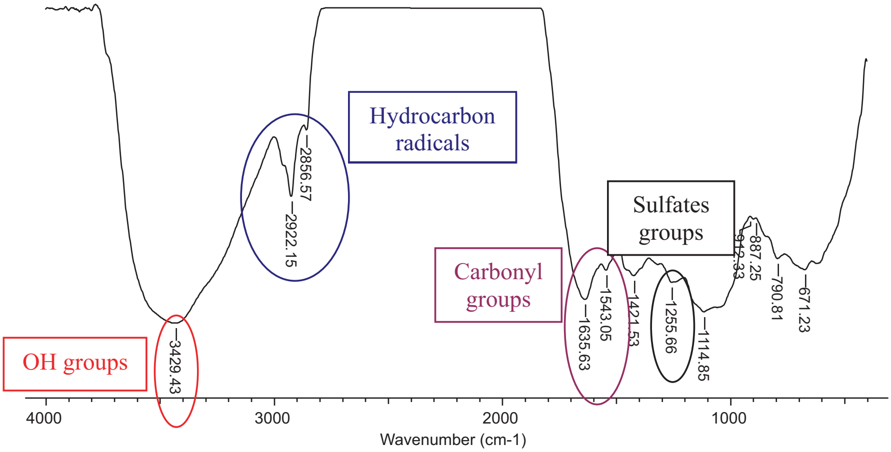

Fig. 4.1 FTIR spectrum of *Ulva lactuca* marine algae. (Adapted after Lupea et al. 2012a)

Table 4.4 The content of alkaline and alkaline earth metal ions of some marine algae (Simionescu et al. 1974)

Marine algae		Na, mg/g	K, mg/g	Ca, mg/g	Mg, mg/g
Brown algae	*Fucus visoides*	173.05	42.71	20.03	12.11
	Cystoseira barbata	145.0	86.61	27.31	10.0
Red algae	*Gracilaria compressa*	49.01	50.81	33.12	7.75
	Gracilaria confervoides	32.75	0.18	30.51	4.34
Green algae	*Ulva lactuca*	43.17	23.14	31.80	18.91

Many studies from literature have shown that the brown marine algae have the higher ion-exchange capacity compared with red or green marine algae (Romera et al. 2007; Chojnacka 2010; Mazur et al. 2018). This characteristic is mainly due to the high content of alginate (10–40%) and fucoidan (5–20%) in their structure (Michalak et al. 2013) which determines the presence of a higher number of functional groups on their surface.

Unfortunately, the use of brown and red marine algae in the biosorption processes of heavy metal ions has an important drawback, which drastically limits their industrial applications. Thus, during biosorption, certain organic compounds from marine algae composition (such as alginate, colour pigments, etc.) can be released into the aqueous media, generating the secondary pollution of the treated effluent and the decrease of marine algae biosorption capacity (Yang and Chen 2008).

Unlike these, in marine green algae, the leaching of organic compounds is insignificant, and therefore the effect of secondary pollution is missing most of the time, but also their biosorption capacity is lower compared with brown and red marine algae (Tobin et al. 1988; Hamdy 2000; Apiratikul and Pavasant 2008). Considering all the aspects discussed in this section, it can be said that in the preparation of marine algae as biosorbents for the removal of toxic heavy metal ions from aqueous media, only a few simple steps are required. Figure 4.2 illustrates the main elementary steps involved in the preparation of marine algae biosorbents.

The harvested marine algae are immediately washed with demineralized water to remove the dissolved salts from their leaves. Otherwise, the dissolved salts will significantly change the ionic strength of the aqueous solutions, and their presence will affect the efficiency of the biosorption process. After washing, the drying of marine algae is done in air, often at ambient temperature, because in this way, the humidity is gradually removed and the surface of the algae particles will be wrinkled and cracked more, which will provide a larger specific surface area. The last

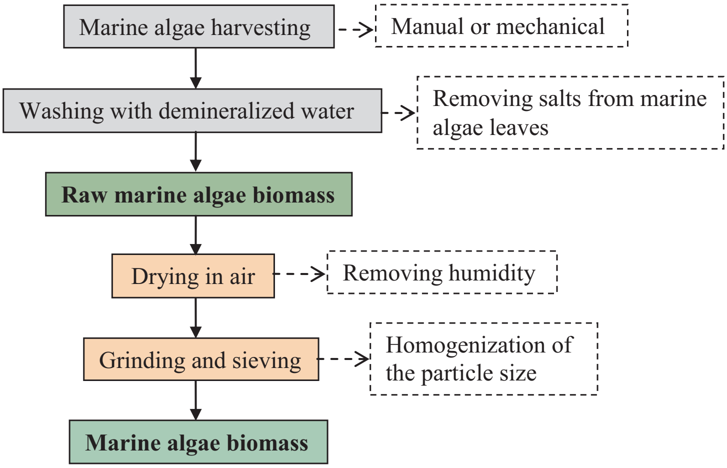

Fig. 4.2 The main steps in the preparation of marine algae biosorbents

important step in the preparation of marine algae biomass is grinding and sieving, which will provide almost the same size of biomass particles.

Under these conditions, the marine algae can be considered “low-cost” biosorbents, which require a few simple steps of preparation and which due to numerous and varied functional groups can be used to design effective biosorption systems to remove toxic heavy metals from aqueous effluents.

4.4 Marine Algae Biosorbents for Removal of Toxic Heavy Metals

As shown in the previous paragraph, the marine algae biomasses have in their composition different organic compounds (such as carbohydrates, proteins, lipids, etc.) that possess numerous and varied functional groups. These functional groups represent the binding sites for toxic heavy metal ions during of biosorption. Under these conditions, the efficiency of biosorption processes will mainly depend on the efficiency of functional groups – heavy metal ion interactions – and this will be affected by:

- The dissociation degree of functional groups
- The speciation form of toxic heavy metal ions
- The number of binding sites form biomass surface
- The contact time between marine algae biomass (solid) and heavy metal ions (aqueous solution)
- Temperature

All these factors will define the experimental conditions in which the biosorption process is carried out, and hence the finding of optimal experimental conditions will ensure the maximum efficiency of the biosorption process. Only when the optimal experimental conditions have been selected (on the basis of experimental and/or computational studies), the biosorption process can be assessed and can be determined by the biosorptive performance of marine algae biomass for a given metal ion.

4.4.1 Selection of Optimal Conditions for the Biosorption Process

It is well known that the retention of metal ions from aqueous media by biosorption using marine algae biosorbents takes place with maximum efficiency only in certain experimental conditions (Donmez et al. 1999; Febrianto et al. 2009; Robals et al. 2016). The most important experimental parameters to be considered when determining the optimal conditions for the biosorption process are:

(i) *Initial solution pH* – because its value depends on the speciation form of toxic heavy metal ions in aqueous solution and the dissociation degree of functional groups from marine algae biomass surface.

(ii) *Biomass dosage* – the amount of marine algae biomass used to remove toxic heavy metal ions from a given volume of aqueous solution determines the number of active sites that may be involved in the biosorption process, and the value of this parameter is important both from economical and technological considerations.

(iii) *Contact time* – an optimal value of this parameter indicates the minimum time required to achieve the interactions between heavy metal ions and superficial functional groups of marine algae biomass and plays an important role in the kinetics modelling of biosorption process.

(iv) *Temperature* – the finding of optimal value of this parameter is important both theoretical considerations, as it allow for the thermodynamic modelling of the biosorption processes, as well as for applicative considerations, because its value can significantly influence the cost of biosorption processes.

Even if in literature the initial heavy metal concentration is considered another experimental parameter that affects the efficiency of biosorption process, its influence is more theoretically important for the modelling of biosorption processes than from a practical point of view because it is well known that in the case of industrial effluents, the concentration of the heavy metal ions varies in a fairly narrow range and their composition is complex.

The effect of each of these experimental parameters on the biosorption efficiency must be analyzed one by one, and the obtained results will allow the selection of the optimal conditions for that the biosorption process takes place with maximum efficiency for a certain toxic heavy metal ion and a certain marine algae biosorbent. Several examples of optimal experimental conditions established for the biosorption of various heavy metal ions on different marine algae biosorbents are summarized in Table 4.5.

Initial solution pH is one of the most important experimental parameters that affects the efficiency of biosorption processes, because its value determined not only the dissociation degree of functional groups from marine algae biomass surface but also the speciation and availability of heavy metal ions to participate at biosorption process (Marques et al. 2000; Esposito et al. 2002). As can be seen from Table 4.5, most of biosorption processes of heavy metal ions on marine algae biosorbents take places with a maximum efficiency at an initial solution pH between 4.0 and 6.0. Obtaining the maximum efficiency of biosorption processes in such a narrow pH range can be explained on the basis of the following considerations:

- *At low pH* (pH < 4.0) – even if most heavy metal ions are predominantly as free as positively charged cations (M^{n+}) in aqueous solution, functional groups in the surface area of marine algae biomass are largely non-dissociated or positively charged, which makes chemical interactions not happen due to the electrostatic repulsive forces. Only the metal ions which exist in the solution as negatively charged species (oxo-anions) can be retained by the marine algae biomass at a very low initial solution pH (Murphy et al. 2008). It is the case of Cr(VI) ions biosorption, for which the optimal pH value is obtained in the pH range of 0.5–1.5 (see Table 4.5), regardless of the type of marine algae biosorbent.

Table 4.5 The experimental conditions selected as optimal for the removal of heavy metal ions by biosorption on marine algae biomass

Metal ion	Marine algae biomass		Optimal experimental conditions for biosorption				References
			pH	Dosage, g/L	t, min	Temperature, °C	
Cu(II)	Green algae	*Ulva fasciata*	5.5	1.0	30	22	Karthikeyan et al. (2007) and Kumar et al. (2006)
		Chaetomorpha linum	5.0	2.0	120	23	Ajjabi and Chouba (2009)
		Spirogyra spp.	5.0	1.0	30	Ambient temp.	Lee and Chang (2011)
	Red algae	*Asparagopsis armata*	5.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Chondrus crispus	4.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Ceramium rubrum	6.0	4.0	90	35	Egel and Doner 2013
	Brown algae	*Fucus vesiculosus*	5.0	1.0	120	23	Mata et al. (2008)
		Sargassum sp.	5.5	1.0	30	25	Karthikeyan et al. (2007)
		Fucus spiralis	5.0	0.5	120	Ambient temp.	Romera et al. (2007)
	Green algae	*Ulva lactuca*	5.0	0.1	60	20	Sari and Tuzen (2008a) and Lupea et al. (2012a)
		Chlorophyta sp.	4.0	4.0	30	25	Sulaymon et al. 2013
		Caulerpa fastigiata	5.5	10.0	60	25	Sarada et al. 2014
	Red algae	*Ceramium virgatum*	5.0	0.1	60	20	Sari and Tuzen (2008b)
		Kappaphycus alvarezii	4.5	2.0	45	32	Praveena and Vijayaraghavan (2015)
		Corallina mediterranea	5.0	10.0	60	25	Ibrahim (2011)
	Brown algae	*Fucus serratus*	4.5	2.5	25	25	Herrero et al. (2006)
		Saccorhiza polyschides	4.5	2.5	> 60	25	Lee and Chang (2011)
		Cystoseira baccata	4.5	2.5	17	25	Lodeiro et al. (2006)
Cr(VI)	Green algae	*Ulva lactuca*	1.0–1.5	3.0	120	25	El-Sikaily et al. (2007)
		Ulva compressa	2.0	2.0	120	Ambient temp.	Murphy et al. (2008)
		Cladophora albida	2.0	4.0	30	25	Deng et al. (2009)
	Red algae	*Palmaria palmate*	2.0	2.0	30	Ambient temp.	Murphy et al. (2008)
		Polysiphonia lanosa	2.0	2.0	30	Ambient temp.	Murphy et al. (2008)
		Ceramium virgatum	1.5	0.1	90	20	Sari and Tuzen (2008c)
	Brown algae	*Fucus vesiculosus*	2.0	2.0	120	Ambient temp.	Murphy et al. (2008)
		Fucus spiralis	2.0	2.0	120	Ambient temp.	Murphy et al. (2008)

(continued)

Table 4.5 (continued)

Metal ion	Marine algae biomass		Optimal experimental conditions for biosorption				References
			pH	Dosage, g/L	t, min	Temperature, °C	
Ni(II)	Green algae	*Ulva lactuca*	4.5	2.0	60	30	Zakhama et al. (2011)
		Cladophora spp.	5.0	5.0	–	23	Zakhama et al. (2011)
		Codium vermilara	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
	Red algae	*Asparagopsis armata*	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Chondrus crispus	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Kappaphycus alvarezii	4.5	2.0	45	32	Praveena and Vijayaraghavan (2015)
	Brown algae	*Padina australis*	6.0	1.0	120	30	Kalyani et al. (2004)
		Fucus spiralis	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Ascophyllum nodosum	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
Pb(II)	Green algae	*Ulva lactuca*	5.0	8.0	30	22	Bulgariu et al. (2010)
		Cladophora fasci.	5.0	2.0	30	25	Deng et al. (2007)
		Spirogyra spp.	5.0	0.5	100	20	Lee and Chang (2011)
	Red algae	*Asparagopsis armata*	4.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Chondrus crispus	4.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Kappaphycus alvarezii	4.5	2.0	45	32	Praveena and Vijayaraghavan 2015
	Brown algae	*Fucus spiralis*	5.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Ascophyllum nodosum	5.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Fucus vesiculosus	5.0	1.0	120	23	Mata et al. (2008)
Zn(II)	Green algae	*Spirogyra insignis*	6.0	1.0	120	Ambient temp.	Romera et al. (2007)
		Chaetomorpha linum	5.0	20	120	25	Ajjabi and Chouba (2009)
		Ulva fasciata sp.	5.0	0.1	20	30	Kumar et al. (2007)
	Red algae	*Asparagopsis armata*	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Chondrus crispus	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Gracilaria caudata	5.0	1.5	120	25	Cechinel et al. (2018)
	Brown algae	*Fucus spiralis*	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Ascophyllum nodosum	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Laminaria hyperborea	5.0	2.0	45	25	Freitas et al. (2008)

- *At higher pH values* (pH > 6.0) – the functional groups from marine algae biomass surface have a high dissociation degree (most of them becoming negatively charged), but the biosorption process can be prevented by changing the speciation form of heavy metal ions from aqueous solution. This is because at high initial solution pH, the hydrolysis of metal ions can take place and the formed hydrolyzed metallic species no longer have the same availability for biosorption processes (Romera et al. 2007).

The decreasing of the biosorption efficiency at initial solution pH lower than 4.0 and higher than 6.0 can be easily observed in case of some toxic heavy metal ion retention on *Ulva lactuca* marine green algae biomass (Fig. 4.3).

Therefore, choosing an initial solution pH between 4.0 and 6.0 (see Table 4.5) will ensure both a dissociation degree of functional groups of marine algae biomass sufficiently high and an adequate speciation form of the toxic heavy metal ions so that the biosorption process occurs with maximum efficiency.

The quantity of marine algae biomass used as biosorbent for a given volume of aqueous solution with known concentration of toxic heavy metal ions may also influence the efficiency of biosorption processes. For the selection of the optimal biosorbent dosage, it is necessary to analyze the performances of biosorption process, as well as some economic and operational aspects. In the analysis of the biosorption process performances, studies from literature (Gokhale et al. 2008; Farooq et al. 2010; Finocchio et al. 2010) have shown that:

- The removal percent of toxic heavy metal ions from aqueous solution increases with the increasing of marine algae biomass dose, mainly due to the increase of the number of active sites (superficial functional groups) which can bond metal ions from aqueous solution.

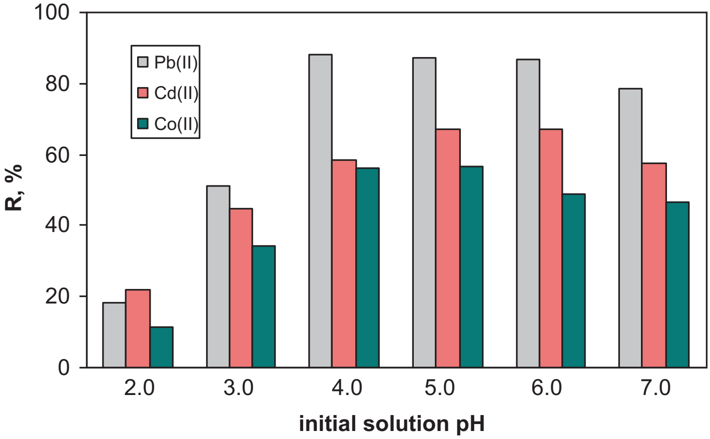

Fig. 4.3 Variation of the biosorption efficiency in function of initial solution pH in case of *Ulva lactuca* marine green algae biomass. (Bulgariu and Bulgariu 2012; Lupea et al. 2012a, b)

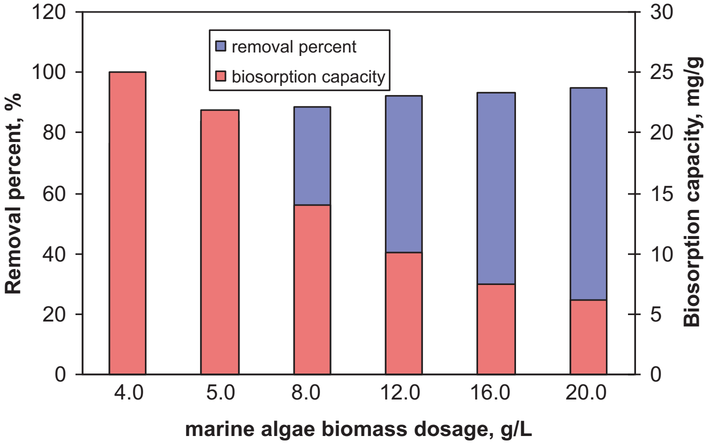

Fig. 4.4 Variation of the biosorption process parameters as a function of biosorbent dosage in case of Pb(II) biosorption on *Callithamnion corymbosum* algae biomass

- The biosorption capacity of marine algae biomass decreases with the increasing of biosorbent dosage due to the fact that the metal ions have more functional groups available for interaction, and this makes the amount of metal ions retained per weight unit of marine algae biomass (which means the biosorption capacity) to decrease.

A suggestive illustration of such opposite variation of these two parameters (biosorption capacity and percent removal) is presented in Fig. 4.4, for the biosorption of Pb(II) ions from aqueous media on *Callithamnion corymbosum* algae biomass (red marine algae).

Therefore, in most of cases, the biosorption of toxic heavy metals requires relatively low quantities of marine algae biomass (see Table 4.5), which will allow for high biosorption performance of marine algae biomass (high values of biosorption capacity) but also a high efficiency of biosorption process (high values of removal percent).

On the other hand, the use of low amounts of marine algae biosorbents in the biosorption processes of toxic heavy metal ions also has several economic and operating advantages, because:

- The low amounts of marine algae biosorbent used in the biosorption processes will reduce the costs and generate low amounts of waste biomass loaded with toxic heavy metal ions, which have been also properly treated so as not to become a danger to the environment.
- Some technological operations, such as mixing, filtration, transport, etc., will require low time and energy consumption.

Biosorption of toxic heavy metals depends largely on contact time. The studies from literature that discuss the kinetics of toxic heavy metal ion biosorption on

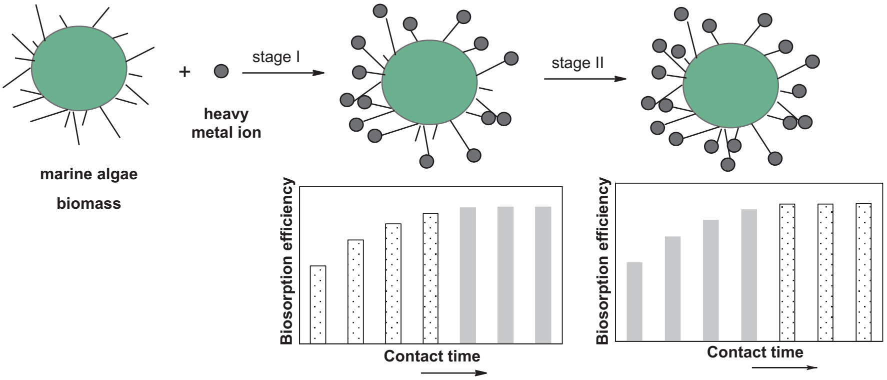

Fig. 4.5 Dependence between the biosorption efficiency and contact time in case of marine algae biosorbents

marine algae biomass (Sheng et al. 2004; Lee and Chang 2011; Zeraatkar et al. 2016) indicate that the biosorption process generally takes place in two stages:

- *Stage I* – rapid stage – in the first 5–30 min, the amount of heavy metal retained on marine algae biomass surface increases sharply, and the values of removal percents can attain 90% from initial concentration of heavy metal ion.
- *Stage II* – slower stage – can take up to 3–4 h, and where the amount of heavy metal ions retained on marine algae biomass surface does not vary by more than 5–10%.

Figure 4.5 presented a typical variation of the biosorption efficiency of toxic heavy metal ions on marine algae biomass in function of contact time.

Such two-step biosorption process of toxic heavy metal ions on marine algae biomass can be explained as (Qin et al. 2006; Gerente et al. 2007; Febrianto et al. 2009):

- *In stage I* – all superficial functional groups of marine algae biomass are free and geometrical available for to interact with heavy metal ions from aqueous solution. Therefore, the electrostatic interactions can easily occur, and the ion-exchange processes are effective in the binding of heavy metal ions on the surface of marine algae biomass.
- *In stage II* – majority of superficial functional groups are already occupied, and the heavy metal ions should find the superficial groups within the pores of marine algae biomass particle to interact. In this case, the elementary diffusion process became the rate-limiting step, and the efficiency of biosorption process does not vary significantly.

The fast biosorption of toxic heavy metal ions on marine algae biomass (see Table 4.5) has very important practical and economical consequences, because it allows the scale-up of the biosorption process on industrial scale, which will ensure high efficiency and low cost of operating (Liu et al. 2009).

Temperature can influence the efficiency of toxic heavy metal ion biosorption on marine algae biomass but to a much lower extent than the other experimental parameters mentioned above. This is because the rise of temperature must be done only up to 50–60 °C, in order to prevent the degradation of marine algae biomass, and under these conditions, the variation of the biosorption capacity is most often quite small for the biosorption of most heavy metal ions (Monteiro et al. 2010; Johansson et al. 2016). But, in function of the nature of marine algae biomass used as biosorbent and the type of toxic heavy metal from aqueous solution, the increase of temperature can determine:

- *The increase of the biosorption capacity* – which means that the biosorption process is of endothermic nature (Gupta and Rastogi 2008; Romera et al. 2007; Johansson et al. 2016)
- *The decrease of the biosorption capacity* – indicating an exothermic nature of the biosorption process (Cruz et al. 2004; Sari and Tuzen 2008a)
- *Insignificant changes of the biosorption capacity* (Martins et al. 2004; Lodeiro et al. 2006; Lupea et al. 2012a)

However, by comparing the variation in biosorption capacities and the costs required for temperature rise, in most cases the ambient temperature is considered to be optimal (see Table 4.5), especially for economic reasons (Wang and Chan 2009).

4.4.2 Biosorptive Performances of Marine Algae Biosorbents

The retention of toxic heavy metal ions on marine algae biomass through biosorption is a non-metabolically process, in which the metal ions are bonded on marine algae surface by ion-exchange, superficial complexation, adsorption, coordination, or micro-precipitation (Febrianto et al. 2009). Therefore, the biosorption can be considered a physicochemical process, whose efficiency is mainly dictated by the elementary interactions between functional groups of marine algae biosorbents and toxic heavy metal ions from aqueous media.

As it was already mentioned in the previous paragraphs, the constituents of marine algae biomass provide various functional groups (such as hydroxyl, carboxyl, carbonyl, sulphonic, etc.), which represent the binding sites and which determine the retention of toxic heavy metal ions from aqueous media, through specific interactions. In optimal experimental conditions (pH and biosorbent dosage), most of these functional groups are dissociated and will generate negative charges on the marine algae biomass surface. These negative charges are responsible for the electrostatic interactions with metal ions from aqueous solution (Murphy et al. 2008; Mazur et al. 2018). Therefore, the toxic heavy metal ions will be retained by marine algae biomass, and most of the studies from literature indicate that such biosorption process occurs until to the formation of complete monolayer coverage, according with Langmuir isotherm model (Chong and Volesky 1995; Rangabhashiyam et al. 2014). The number and availability of functional groups from marine algae biomass surface will dictate the efficiency of the biosorption process in selected optimal experimental conditions, and the parameter used for the quantitative evaluation of this efficiency is the maximum biosorption capacity (q_{max}, mg/g). The maximum biosorption capacity indicates the maximum amount of toxic heavy metal ions retained on weight unit of marine algae biomass and may be calculated from linear Langmuir equation (Rangabhashiyam et al. 2014).

On the other hand, the toxic heavy metal ions from aqueous solution have different affinities for the functional groups of marine algae biomass. In the optimal experimental conditions (pH, contact time) selected so that such interactions to be facilitated, the heavy metal ions will be retained on marine algae biomass the easier as their affinity for the functional groups present on the biosorbent surface will be greater. The ease with which metal ions interact with functional groups of marine algae biomass may be evaluated by kinetics modelling of the biosorption process, and the quantitative parameter used in this case is constant rate (which represents the amount of toxic heavy metal ions retained on mass unit of biosorbent in time unit).

Most of the biosorption processes which use marine algae biosorbents follows a pseudo-second order kinetics model, and under these conditions, the rate constant is calculated from the linear pseudo-second-order kinetics equation (Febrianto et al. 2009; Ibrahim 2011). This means that for the retention of a heavy metal ion, two binding sites are required (Chojnacka 2010), and therefore beside the number, the geometrical availability of functional groups from marine algae biomass surface will significantly affect the performances of the biosorption processes.

Starting from these observations, always in assessing the performance of biosorption processes should be considered the values of maximum biosorption capacity (which is a measure of the availability of marine algae biomass to participate at the biosorption processes) and of kinetics constant rate (which indicate the affinity of metal ions from aqueous solution to interact with the functional groups of biosorbent). Several examples in this regard are shown in Table 4.6.

The values presented in Table 4.6 show that, in most of cases, the brown marine algae biomass showed higher biosorptive performances in the removal processes of different toxic heavy metal ions, compared with red or green marine algae biomass. The high biosorption capacity of brown marine algae biomass has been attributed to the presence of high concentration of alginate in their cell walls, which is mainly responsible by such high toxic metal ions removal ability (Mazur et al. 2018). Thus, Romera et al. (2007) have shown that the affinity of toxic heavy metal ions to alginate (or fucoidan) depends by their geometrical radius and follows the order: Pb(II) > Cu(II) > Cd(II) > Zn(II) > Ni(II). This increasing of the biosorption capacity of marine brown algae with the increasing of metal ion radius is a consequence of stereochemical effect, because the metal ions with larger volume can find easier binding site with two distant functional groups, on marine algae surface. Unfortunately, the use of brown marine algae biomass in the biosorption processes of heavy metal ions can cause the contamination of treated aqueous effluent with organic compounds which are released from their composition, during of biosorption. This negative effect of secondary pollution is also undesirable and can be

Table 4.6 Biosorptive performances of different types of marine algae biomass for different toxic heavy metal ions in the biosorption processes

Metal ion	Marine algae biomass		Biosorptive performances		References
			q_{max}, mg/g	k, g/mg min	
Cu(II)	Green algae	*Ulva fasciata* sp.	73.50	0.013	Karthikeyan et al. (2007)
		Spirogyra sp.	38.61	–	Lee and Chang (2011)
		Cladophora sp.	14.71	–	
	Red algae	*Osmundea pinnatifida*	6.94		El Hassouni et al. (2014)
		Gymnogongrus torulosus	51.47	0.019	Areco and dos Santos Afonso (2010)
		Pterocladia capillacea	49.50	0.042	El-Sikaily et al. (2011)
	Brown algae	*Fucus serratus*	101.73	0.051	Ahmady-Asbchin et al. (2008) and Mata et al. (2008)
		Undaria pinnatifida	78.88	4.84	Chen et al. (2008)
		Laminaria sp.	61.59	0.024	Liu et al. (2009) and Freitas et al. (2008)
Cd(II)	Green algae	*Oedogonium* sp.	88.20	0.012	Gupta and Rastogi (2008)
		Ulva lactuca	41.66	0.011	Lupea et al. (2012a)
		Chaetomorpha linum	53.96	0.034	Hashim and Chu (2004)
	Red algae	*Gelidium*	18.02	0.086	Vilar et al. (2006)
		Ceramium virgatum	39.70	0.003	Sarı and Tuzen (2008b)
		Gracilaria edulis	26.98	0.026	Hashim and Chu (2004)
	Brown algae	*Laminaria* sp.	104.53	0.024	Delle (2001) and Freitas et al. (2008)
		Cystoseira baccata	77.56	0.007	Lodeiro et al. (2006)
		Undaria pinnatifida	121.40	0.002	Plaza Cazón et al. (2013)
Cr(VI)	Green algae	*Caulerpa racemosa*	0.57	0.011	Pandya et al. (2017)
		Ulva lactuca	55.55	0.024	
		Oedogonium sp.	35.41	0.212	Bakatula et al. (2014)
	Red algae	*Ceramium virgatum*	26.50	0.024	Sarı and Tuzen (2008c)
		Palmaria palmate	33.80	–	Murphy et al. (2008)
		Polysiphonia lanosa	45.76	–	
	Brown algae	*Fucus vesiculosus*	42.64	–	
		Fucus spiralis	35.36	–	
		Bifurcation bifurcata	23.40	1.666	Ainane et al. (2014)

Ni(II)	Green algae	*Oedogonium* sp.	26.18	0.042	Bakatula et al. (2014)
		Ulva sp.	12.91	0.015	Sheng et al. (2004)
	Red algae	*Gracilaria caudata*	50.10	0.066	Bermudez et al. (2011)
		Gracilaria sp.	16.10	0.011	Sheng et al. (2004)
	Brown algae	*Laminaria* sp.	66.33	0.167	Liu et al. (2009)
		Sargassum glaucescens	52.63	0.102	Pahlavanzadeh et al. (2010)
		Cystoseira indica	47.62	0.022	Pahlavanzadeh et al. (2010)
Pb(II)	Green algae	*Cladophora* sp.	200.42	0.012	Deng et al. (2007)
		Oedogonium sp.	144.92	0.064	Gupta and Rastogi (2008)
		Caulerpa fastigiata	17.51	0.083	Sarada et al. (2014)
	Red algae	*Gymnogongrus torulosus*	140.89	0.011	Areco and dos Santos Afonso (2010)
		Jania rubens	30.6	0.012	Ibrahim (2011)
		Pterocladiella capillacea	34.1	0.011	
	Brown algae	*Lobophora* sp.	580.16	–	Jha et al. (2009)
		Cystoseira baccata	182.33	0.001	Lodeiro et al. (2006)
		Laminaria japonica	213.42	0.020	Luo et al. (2006) and Freitas et al. (2008)
Zn(II)	Green algae	*Ulva fasciata* sp.	13.50	0.168	Kumar et al. (2007)
		Ulva lactuca	31.05	0.092	Badescu et al. (2017)
		Oedogonium sp.	36.55	0.038	Bakatula et al. (2014)
	Red algae	*Gymnogongrus torulosus*	44.46	0.022	Areco and dos Santos Afonso (2010)
		Gracilaria sp.	26.15	0.023	Sheng et al. (2004)
		Jania rubens	25.81	0.021	Ibrahim (2011)
	Brown algae	*Laminaria* sp.	54.26	0.075	Freitas et al. (2008)
		Sargassum muticum	49.63	0.012	Freitas et al. (2008)
		Undaria pinnatifida	10.46	0.024	Plaza Cazón et al. (2013)

minimized by a preliminary treatment of brown marine algae biomass with dilute solutions of alkali.

In case of red algae, the sulphated polysaccharides (galactanes) were found to be mainly responsible for the retention of toxic heavy metal ions from aqueous solution, often by electrostatic interactions (ion exchange or superficial complexation) (Romera et al. 2007). This kind of algae will prefer to retain toxic heavy metal ions with high affinity for O-donor groups, such as Pb(II), Cu(II), or Ni(II) (see Table 4.6). And in case of red marine algae biosorbents, the secondary pollution can be observed, but its intensity is lower compared with brown marine algae biomass, and can be minimized in the same way.

The green algae have in their composition numerous carboxyl, hydroxyl, sulphate, phosphate and amine groups from α-, β- and γ-carotenes and several xanthophylls (Gupta and Rastogi 2008) and will bind the heavy metal ions from aqueous solution, predominantly through ion-exchange interactions. This kind of interactions is not selective, and therefore the biosorption capacity of green marine algae are significantly influenced by the presence of other metal ions in aqueous solution (Hashim and Chu 2004; Gupta and Rastogi 2008; Pandya et al. 2017). However, it should be noted that in case of marine green algae biomass, the intensity of the secondary pollution effects is much lower compared with red and brown marine algae biomasses and that due to the high number of amino groups from their structure have the best performances in the retention of Cr(VI) ions, if the experimental conditions are adequate (see Table 4.6).

4.5 Regeneration and Recycling of Exhausted Marine Algae Biomass

The evaluation of the biosorptive performances of marine algae biomass in the removal processes of toxic heavy metal ions from aqueous effluents is not complete without the studies related to the regeneration and recycling of exhausted biosorbents. This is because the possibility to use the same quantity of marine algae biomass in multiple biosorption processes offers important environment and economic benefits. The chemical process involved in this case is named desorption, and suppose the mixing of exhausted marine algae biomass with a desorption agent, in certain experimental conditions (contact time, exactly known volume and concentration of desorption agent, temperature, etc.), when the retained toxic heavy metal ions are replaced by other ions of desorption agent structure (Lasheen et al. 2012; Robalds et al. 2016; Kolodynska et al. 2017). The elementary processes that occur in desorption of toxic heavy metal ions from exhausted marine algae biomass are mainly ion-exchange type (Fig. 4.6), and suppose the release of retained toxic heavy metal ions in aqueous solution concomitant with the regeneration of marine algae biomass. Because the released toxic metal ions can be recovered and reintroduced in the industrial activities and that the regenerated biosorbent can be used in another

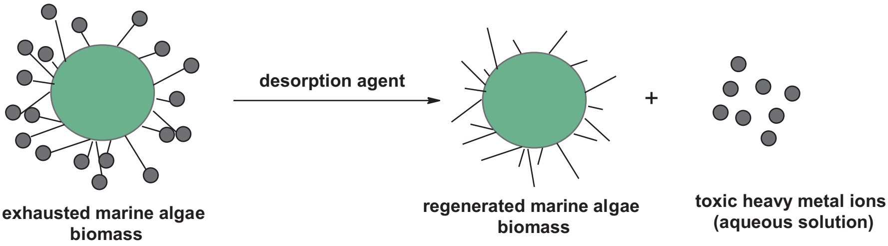

Fig. 4.6 Schematic illustration of the toxic heavy metal ions desorption from exhausted marine algae biomass

biosorption cycle, desorption will contribute to lowering the costs of removing toxic heavy metal ions from aqueous media.

The quantitative desorption of the toxic heavy metal ions retained on marine algae biomass and the regeneration of biosorbents can be done using various chemical reagents, such as mineral acids (HCl, HNO_3, etc.), inorganic salts (NaCl, $NaNO_3$, KNO_3, $CaCl_2$, etc.), or complexing agents (EDTA), in various experimental conditions (Gupta et al. 2015; De Gisi et al. 2016; Tran and Chao 2018). After desorption, the aqueous solution contains the toxic heavy metal ions, which can be recovered through specific procedures, and the solid phase is the regenerated marine algae biosorbent, which is washed, dried and conditioned, in order to be used in another biosorption cycle (Kolodynska et al. 2017). However, for desorption processes to be effective, the following should be considered:

- The solution of desorption agent should have a pH with a least 2–4 units lower than the optimal pH used for the biosorption of heavy metal ions.
- The ratio between the exhausted marine algae biomass and the volume of desorbent solution should be high, so that a low volume of desorbent solution is used to treat the large amount of depleted biosorbent – in this way the costs related to biosorbent regeneration and recovery from the released heavy metal is minimized.
- The concentration of the desorbent solution must be high (10^{-3} – 1.0 mol/l) so that the desorption process is efficient.
- The desorption processes should take place at ambient temperature and only when it is absolutely necessary at higher temperatures – in this way the cost of desorption processes is kept low, and the damage of the regenerated marine algae biosorbents is avoided.

In Table 4.7 are presented several desorption possibilities of toxic heavy metal ions form exhausted marine algae biomass that can be used for the recovery of metal ions and biosorbent regeneration.

Most often, mineral acids such as HCl or HNO_3 are used for the desorption of toxic heavy metal ions from exhausted marine algae biomass (Gupta et al. 2015; Tran and Chao 2018), because they (i) have high efficiency in desorption processes (95–97%) compared with inorganic salts (see Table 4.7) and (ii) facilitate the

Table 4.7 Characteristics of some desorption processes used for the treatment of exhausted marine algae biomass loaded with toxic heavy metal ions

Metal ion	Marine algae biomass	Desorption agent	Metal recovery, %	References
Cd(II)	*Ulva lactuca*	0.1 M HCl	> 98	Lupea et al. (2012a)
	Oedogonium sp.	0.5 M HCl	84.80	Gupta and Rastogi (2008)
Cu(II)	*Halimeda gracilis*	0.2 M HCl	88.13	Jayakumar et al. (2015)
Cr(VI)	*Halimeda gracilis*	0.2 M HCl	98.02	Jayakumar et al. (2014)
Pb(II)	*Sargassum* sp.	0.1 M HNO_3	> 95	Martins et al. (2006)
Zn(II)	*Scenedesmus* sp.	0.1 M H_2SO_4	98.40	Sarwa and Verma (2014)
	Fucus vesiculosus	1 N HNO_3	≈ 100	Castro et al. (2017)
Cu(II)	*Gracilaria caudata*	0.5 M $CaCl_2$	38.00	Cechinel et al. (2018)
		0.5 M NaCl	90.00	
Ni(II)	*Gracilaria caudata*	0.5 M $CaCl_2$	58.00	
		0.5 M NaCl	52.00	
Zn(II)	*Gracilaria caudata*	0.5 M $CaCl_2$	100	
		0.5 M NaCl	59.00	
	Ulva lactuca	0.1 M NaCl	78.60	Badescu et al. (2017)
		0.1 M $CaCl_2$	92.00	
Pb(II)	*Sargassum* sp.	0.1 M EDTA	95.00	Martins et al. (2006)

recovery of the desorbed metal ions, which are found in aqueous solution as simple chemical species, compared with complexing agents (when the desorbed metal ions are released in aqueous solution as complex species, which make their recovery to be more difficult) (Martins et al. 2006).

However, the efficiency of the regenerated marine algae biomass in the biosorption processes of toxic heavy metal ions decreases as the number of biosorption/desorption cycles increases (Gautam et al. 2015; Cechinel et al. 2018; Tran and Chao 2018). This makes that in most cases, the use of marine algae biomass is not efficient after 6–8 repeated use (Table 4.8).

The loss in the biosorption efficiency of regenerated marine algae biomass in superior cycles is probably caused by (Gautam et al. 2015; Zeraatkar et al. 2016):

- Incomplete desorption of toxic heavy metal ions – if the desorption agent is not suitable or he does not have a well-chosen concentration, not all the toxic metal ions retained by biosorption are released in the desorption processes, and so some functional groups from marine algae biomass surface are not released after desorption.
- After several treatments of exhausted marine algae biomass with concentrated solution desorption agents, the structure of biomass can be irreversibly degraded, due to the low mechanical resistance of marine algae biomass that results in a decrease in the number of functional groups available for toxic heavy metal biosorption.

Table 4.8 Decreasing of biosorption efficiency (% loss) of marine algae biomass in multiple biosorption/desorption cycles of toxic heavy metal ions

Metal ion	Marine algae biomass	Desorption agent	No. cycles	% loss	References
Cd(II)	*Ulva lactuca*	0.1 M HCl	3	32.10	Lupea et al. (2012a)
	Oedogonium sp.	0.5 M HCl	5	27.70	Gupta and Rastogi (2008)
Cu(II)	*Halimeda gracilis*	0.2 M HCl	2	18.30	Jayakumar et al. (2015)
Cr(VI)	*Halimeda gracilis*	0.2 M HCl	10	18.40	Jayakumar et al. (2014)
Cu(II)	*Ulva lactuca*	0.1 M H_2SO_4	3	43.40	Lau et al. (2003)
Ni(II)	*Ulva lactuca*	0.1 M H_2SO_4	3	32.80	
Zn(II)	*Ulva lactuca*	0.1 M H_2SO_4	3	46.60	
Cu(II)	*Gracilaria caudata*	0.5 M $CaCl_2$	2	29.00	Cechinel et al. (2018)
Ni(II)	*Gracilaria caudata*	0.5 M $CaCl_2$	2	11.00	
Zn(II)	*Gracilaria caudata*	0.5 M $CaCl_2$	2	36.00	

Unfortunately, these two major disadvantages (incomplete desorption of toxic heavy metal ions and gradual degradation of the marine algae biomass after each biosorption/desorption cycles) have an important contribution to the limitation of practical applicability of marine algae biosorbents in the removal processes of toxic heavy metal ions from aqueous media on a large scale. Therefore, finding new ways for the valorization of the exhausted marine algae biomasses loaded with toxic heavy metal ions is still an open issue for research.

4.6 Conclusions and Final Remarks

However, the use of marine algae biomass as biosorbents for the removal of toxic heavy metal ions has several important advantages, such as the following:

- Are cheap and available in many regions of the world.
- Their cultivation does not require agricultural soil, so they do not compete with agricultural crops.
- Requires only a few easy and simple stages for preparation.
- Have in their structure various functional groups that easily bind toxic heavy metal ions from aqueous media.

For these low-cost materials have found only few industrial applications at this time.

This is due to the fact that the use of marine algae biomass as biosorbent in the removal processes of toxic heavy metal ions has two important drawbacks, namely, the biosorptive performances of marine algae biomass are lower than the the ion-exchange resins, and the marine algae biomasses have low mechanical resistance and short duration of use, which are responsible for the limited applicability of these versatile materials in the treatment of industrial wastewater.

Under these conditions, the further studies related to the marine algae biosorbents should be directed to the finding of:

(i) Adequate treatments of marine algae biomass that allow for increased of their biosorption capacity and thus to improve their biosorptive performances.
(ii) Adequate immobilization procedures of marine algae biomasses on various supports (often polymeric), which will increase their mechanical strength and life of utilization.

However, the use of marine algae biomass as biosorbent in the advanced treatment of wastewater containing heavy metal ions could be a helpful solution for the efficient treatment of industrial effluents.

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Chapter 5
Cost-Effective Green Materials for the Removal of Pesticides from Aqueous Medium

Nazia Tarannum and Rizwan Khan

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Abstract The greatest threat to the world is water contamination which may be due to geological or anthropogenic (man-made) reasons. Water pollution has affected the life of plants and animals directly or indirectly. The common water contamination resources are civilization, industrialization, environmental changes, agricultural activities and global changes. The chemistry is integrated in a constructive approach to provide healthy life along with ethical and economic environmental concerns. The most easily affected source of pesticide contamination is water which directly or indirectly affects our ecosystem. The major health-related issues are caused mainly by water contamination. The chapter emphasizes the comprehensive view of application of green materials and their processes for pesticide remediation. Seeing the harmful effect of the pesticide on environment, ecosystem and human

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N. Tarannum (✉) · R. Khan
Department of Chemistry, Chaudhary Charan Singh University, Meerut, Uttar Pradesh, India

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health, the need of the day is to use green materials for removing pesticides. These green materials are economic and readily available and may be regenerated after use without imposing pollution issues. Different sources of green materials readily used in water treatment for pesticides are carbonaceous adsorbents, bioadsorbents, agriculture waste adsorbents, industrial waste adsorbents, nanomaterial-based adsorbents, etc.

Keywords Cost-effective · Wastewater treatment · Pesticides · Green materials · Bioadsorbents

5.1 Introduction

The sustenance of life is impossible without water. The marine water is the major part of the earth which is not used without processing. The groundwater is the only available source for drinking purposes. However, this percentage is sufficient to fulfil the needs of all living beings. The water quality that is used is the subject of concern since it supports physiological activities of living cell (Agrawal et al. 2010). The appropriate quantity and quality of water add to the economy of the world. The growing industries and advancement of technology have posed danger to water resources throughout the world. About one-sixth of the population of the world faces the challenge of unavailability of freshwater (Shahat et al. 2015; Elimelech 2006). The major part of public water supply in India is comprised of groundwater. According to the world health report 1998, the availability of water supply varies with respect to region and state. In the 1970s, among 2.5 billion people in developing world, only 38% has available safe drinking water. In the early 1980s, the approximate coverage of supply of water was 75% in urban areas and about 46% in rural areas. The developing countries with 75% of the growing population have access to water supply due to which the population is prone to water-borne disease (Kumar et al. 2017).

The greatest threat to the world is water contamination which may be due to anthropogenic or geological reasons (Fawell and Nieuwenhuijsen 2003). Water pollution has affected the life of plants and animals directly or indirectly. The common water contamination resources are civilization, industrialization, environmental changes, agricultural activities and global changes. The major cause is the discharge from the industries which are exposed to water bodies without proper treatment of harmful constituents (Awual et al. 2015). Water contamination because of organic pollutants is dangerous due to carcinogenic nature (Yang 2011). The kind of pollutants released in water depends mainly on the industry. The common regular pollutants acting as effluents are dyes, phenols, pesticides, metal ions, detergents, insecticides and organic aromatic compounds and chemicals (Nabi et al. 2007; Pathania et al. 2015).

In the past few decades, contamination of water resources by pesticide has evolved as a vital environmental concern due to prolonged exposure and low-dose effects on aquatic lives and public health (Sudo et al. 2002). The immense application of pesticides in agriculture has led to ground- and surface water contamination through runoff, drift, leaching and drainage. The consumption of contaminated surface water may have adverse ecotoxicological consequences on aquatic flora and fauna and human health (Forney and Davis 1981; Mulla and Mian 1981). The acephate exposure has caused major shifts in biochemical and haematological profile (Kulkarni and Bhikave 2015). Furthermore, the exposure of endosulfan residues as occupational health concern has caused health issues (Bedi et al. 2015). The excessive use of insecticide like acephate has long persistence in soil causing environmental pollution (Rodriguez-Gonzalo et al. 2010). Methamidophos is the pesticide commonly used in the field which has high chance of water contamination due to its high solubility and water runoff property. Thereby, the user needs to be educated about proper management of the use of pesticide (Fuller and Sudha Chaithanya 2015). Apart from this, heavy metal-based pesticides are adding to the pollutants (Pastircakova 2004; Demirbas et al. 2005). The heavy metal ions are not degraded and act as a persistent environmental contaminant harmful to aquatic life and human health (Peternele et al. 1999).

Several research reports have proposed different methods for the pesticide removal from water. Although, the wide spectrum of pesticides used has made this area of research ardous for proposing one technique for unanimous removal of pesticides. Several methods presented in the literature for pesticide removal are as such: combined photo-Fenton and biological oxidation (Martın et al. 2008), photocatalytic degradation (Aungpradit et al. 2007; Mahalakshmi et al. 2007), advanced oxidation processes (Saritha et al. 2007), aerobic degradation (Murthy and Manonmani 2007), ozonation (Maldonado et al. 2006), nanofiltration membranes (Ahmad et al. 2008), coagulation (Jia et al. 2006), fluid extraction (Lagadec et al. 2000), solid-phase extraction (Masselon et al. 1996) and adsorption (Dabrowski 2001; Danish et al. 2010; Rafatullah et al. 2010a, b). Nowadays, researchers are attracted to the production of cost-effective adsorbents to substitute expensive wastewater treatment methods like chemical precipitation, ion exchange, adsorption, electroflotation, membrane separation, reverse osmosis, electrodialysis, solvent extraction, etc. (Alothman et al. 2013). Among these methods, physio-chemical process (adsorption) is quite efficient in the removal of heavy metals from water. Bailey et al. (1999) discussed that an adsorbent is considered low cost if it is abundant in nature, needs less processing and is readily available by-product of waste material. The wastes from plants are inexpensive and have low economic value, for example, papaya wood (Saeed et al. 2005), maize leaf (Babarinde et al. 2006), walnut shells (Memona et al. 2014), teak leaf powder (King et al. 2006), bagasse, sawdust (Sharma et al. 2008), rice husk ash (Saha et al. 2015), sky fruit husk activated carbon (Njoku et al. 2014), watermelon peels (Memon et al. 2008), peanut hull pellets (Johnson et al. 2002), tea leaves (Islam et al. 2009), coconut shell charcoal (Sharma et al. 2008), sunflower seed shells (Rojas et al. 2014), horseshoe sea crab shell (Gulen et al. 2005), etc.

This chapter deals with the review of literature of the problem related to wastewater generated due to exposure of different pollutants especially pesticides and state-of-the-art and cost-effective methods proposed for the treatment of wastewater. It deals with green material used for treatment due to its natural abundance, slight processing methods, high economic state and regeneration ability.

5.2 Different Kinds of Pollutants Found in Water Including Pesticides

Water pollution has deteriorated the physical and chemical properties of water making it unfavourable to utilize for daily purpose. Water pollution may have two forms: first one is due to the change in the type and amount of materials conceded by water, and the other one is due to alternation of the physical characteristics of water body (Gupta et al. 2009). There are different sources of water pollution like mining, landfills, petroleum drilling and agriculture lands. Other sources include human activities like sanitary sewers, industry and construction work. However, the increase in agricultural, domestic and industrial activities have resulted in the release of toxic pollutants in water (Bushra et al. 2017). Water contamination may be anthropogenic and corgeological (Fawell and Nieuwenhuijsen 2003). The high percentage of toxic pollutants in clean water may lead to acute health problems. The types of natural contaminants taken up by groundwater rely on the characteristics of geological materials of their origin, for example, groundwater flowing through sedimentary soil accept a wide variety of compounds like calcium, magnesium, iron, arsenic, chloride, floride and nitrate (Liu et al. 2005; Harvey et al. 2005; Rukahand Alsokhny 2004; Mulligan et al. 2001; Maheshwari Meenakshi 2006). Other toxic and lethal contaminants are generated by man-made industrial by-products, including heavy metals like copper, mercury, chromium, lead and toxic chemicals, dyes and inorganic and organic compounds like fertilizers and insecticides. Improper disposal of paints, solvents, oils, disinfectants, synthetic detergents, chemicals, medicines, batteries, pesticides, diesel fuel and gasoline may lead to contamination of groundwater (Kass et al. 2005; Yaqout 2003). As per the report of the UN 2003, about two million tons of industry, sewage and agricultural wastes are released in water each day.

Basically, the contaminants associated with water pollution are of three types:

1. Organic contaminants
2. Inorganic contaminants
3. Biological contaminants

5.2.1 *Organic Contaminants*

The sources of anthropogenic organic contamination released to water bodies are industrial wastes, pesticides, domestic waste, etc. The contamination contributed by organic chemical wastes may lead to health issues like cancers, nervous system disorder and hormonal disruptions (Harvey et al. 1984; Ram et al. 1990). Trihalomethanes (THMs), a commonly found contaminant in drinking water, are formed as chlorine reacts with organic matter in water. The major organic pollutants that are induced in water are pesticide (Younes and Galal-Gorchev 2000; Damalas and Eleftherohorinos 2011), volatile organic chemical (VoC), organic chemical (Wehrmann et al. 1996), dye (Pagga and Bruan 1986; Sivakumar and Palanisamy 2008), pharmaceuticals (like tetracycline, erythromycin, ciprofloxacin, salbutamol, carbamazepine, Tamiflu, codeine, salicylic acid and chemotherapy drugs such as 5-flurourcil and ifosfamide) and industrial compounds (like chlorinated solvents, including the polyaromatic hydrocarbons, petroleum hydrocarbons, the fuel oxygenate methyl tertiary butyl ether, phthalates, bisphenols and adipates) (Sharma and Bhattacharya 2017).

5.2.2 Inorganic Contaminants

The chemical parameters of water help in determining contaminants added to it. For example, the geographical status plays a vital role in deciding the water hardness (a natural contaminant). The hardness of water depends upon calcium or magnesium content and if it is carbonate or non-carbonate type. If calcium/magnesium contents are added with carbonate ions ($CO3^{-2}$), it is named as carbonate hardness, and when added with other ions, it is called as non-carbonate hardness. In general, 300–400 mg/L hardness is regarded as suitable for drinking purpose. Higher content of salt in water (TDS (500 mg/L) may lead to kidney stone. In addition to hardness, there are other inorganic substances like heavy metals (viz. fluoride, lead, arsenic, copper, chromium, antimony, mercury, cyanide) which contaminate water resource (Environmental Protection Agency, US 2006; Naushad et al. 2016). The chemical-intensive industries discharge heavy metals like Cd, Ni, Cu, As, Cr, Pb and Zn into water bodies. Due to high solubility, heavy metals may be absorbed by living beings and enter the food chain. In this case, these heavy metals are ingested beyond the acceptable concentration causing serious health-related disorders (Babel and Kurniawan 2004).

5.2.3 Biological Contaminants

Water is contaminated biologically by the presence of algae, bacteria, protozoan or viruses. Each of the biological contaminant in water may cause characteristic health-related problems (Daschner et al. 1996). The abundant organism found in water is algae. The excess growth of algae imparts bad taste and odour to water as well as it produces slime growth on the surface carriers. The blue-green algae (*Microcystis*, *Anabaena*, *Aphanizomenon*) liberate toxins to damage the liver, nervous system and skin (Hitzfeld et al. 2000; Rao et al. 2002). Bacteria-contaminated water is pathogenic (Inamori and Fujimoto 2009) and may cause cholera, typhoid, gastroenteritis and dysentery. There are some nonpathogenic bacteria like iron, sulphur and *Crenothrix* which cause odour and taste issues (Rusin et al. 1997; Nwachcuku and Gerba 2004). Few protozoans such as *Giardia* and *Cryptosporidium* have commonly affected rivers, streams and lakes. Moreover water is contaminated with animal faeces and wastewater generated from sewage treatment plants. Hepatitis and polio viruses are commonly reported in the contaminated water (Sharma and Bhattacharya 2017).

5.3 Adverse Biological Effects of Pesticide Intake

Among the contaminants added to water, organic contaminants have posed serious alarm to the public health. In order to fulfil the needs of a growing population, a wide variety of pesticides are used in agriculture fields to increase the food production or to preserve the food. The pesticides are harmful to human or aquatic life (Lu 1995). The research report confirmed the presence of 39 pesticide residues and their metabolites in groundwater from US and Canadian provinces (Hallberg 1989). The permissible amount of pesticide in water depends on the exposure of child and adult; the children are considered to be four times more prone to the pesticide toxicity than adults (Agrawal et al. 2010). The residues of pesticides are found in everyday foods and beverages, like milk, dairy products, water, fruit juices and wine, and in animal feeds. It is to be mentioned here that washing and peeling do not remove the residues of pesticides completely. But in most cases, this concentration does not surpass the predetermined safe levels. The residues of pesticides have known to be detected in breast milk samples leading to prenatal health issues in children (Nicolopoulou-Stamati et al. 2016). The Aral Sea region is one of the largest regional setups of pesticide contamination and health-related problem. The United Nations Environment Programme (UNEP 1993) stated the effects of pesticides on cancer, pulmonary and haematological morbidity, immune system deficiencies and inborn deformities. The pesticide exposure causes several human health effects due to skin contact because of pesticide handling, inhalation of spray and ingestion of pesticide residues in food or in water.

The workers working in farms are at risks of skin contact, absorption and inhalation of pesticides during its preparation and application in the field. The other source of contamination is through food ingested with pesticide residue. The water quality is degraded by pesticide runoff and has two major health impacts on human. The first common effect is the consumption of pesticide-contaminated shellfish and fish, and the second one is the utilization of pesticide-contaminated water. The World Health Organization (1993) has recognized guidelines for 33 pesticides in drinking water. Several environmental and health protection agencies have recognized ‘acceptable daily intake’ (ADI) values which indicate maximum allowable pesticide ingestion in the lifetime of a person without substantial risk to the person. Wang and Lin (1995) reported that substituted phenols and tetrachlorohydroquinone which are toxic metabolites of the biocide pentachlorophenol produced dose-dependent DNA damage. Some of the harmful effects of pesticides are enumerated below:

1. Death of the plant/aquatic life/living beings
2. Tumours and lesions in fish and animals
3. Reproductive failure or impotency
4. Disruption of endocrine (hormonal) system
5. Suppression of immune system
6. Cellular and DNA damage
7. Teratogenic effects
8. Endangered fish health due to low red to white blood cell ratio, undue deposition of slime on fish scales and gills, etc.
9. Intergenerational effects
10. Other physiological effects like eggshell thinning

The effects mentioned above are not due to the exposure of pesticides but may be related to environmental stresses like eutrophication and pathogens (Baker and Wilkinson 1990; Margni et al. 2002). The organochlorine pesticides pose serious health-related issues like endocrine disorders (Mnif et al. 2011; Lemaire et al. 2004), embryonic development defects (Tiemann 2008), lipid metabolism (Karami-Mohajeri and Abdollahi 2011) and hepatic and haematological variations (Freire et al. 2015). The reports have shown carcinogenic adverse effect due to pesticide intake, but the potential of carcinogenic action cannot be underestimated (Jaga and Dharmani 2003; Witczak and Abdel-Gawad 2014; Chourasiya et al. 2015; Robinson et al. 2015;). The studies based on population have exposed probable relations between organophosphorus pesticide exposure and cardiovascular diseases (Hung et al. 2015), harmful effects on the reproductive system of male (Jamal et al. 2015) and on the nervous system of man (Jaga and Dharmani 2003; Rosenstock et al. 1991; Wesseling et al. 2002; Eskenazi et al. 2006), dementia (Lin et al. 2015) and also a growing risk for non-Hodgkin's lymphoma (Waddell et al. 2001). The prenatal organophosphate exposure is correlated to decreased gestational duration (Eskenazi et al. 2004) and several neurological problems reported in children (Rauh et al. 2015).

Another class of pesticide, carbamates (carbofuran, aldicarb and ziram), has been related to endocrine-disrupting activity (Goad et al. 2004; Mnif et al. 2011), possible reproductive disorders (Goad et al. 2004; Jamal et al. 2015) and lethal effects on mitochondrial function and cellular metabolic mechanisms (Karami-Mohajeri and Abdollahi 2011). However, in vitro research study has shown that carbamate pesticides may cause genotoxic and cytotoxic effects in hamster ovarian cells (Soloneski et al. 2015) and may cause necrosis and apoptosis in human immune cells (Li et al. 2011), natural killer cells (Li et al. 2012; Li et al. 2014) and also apoptosis in T lymphocytes (Li et al. 2015).

It is reported that the infants absorb pesticides and their residues and insect repellents more as compared to adults through their skin and respiratory tract (Hallberg 1989). This may lead to changes in behavioural pattern and many more disease syndromes like ataxia, encephalopathy, muscle cramps, seizures, frequent urination and coma (McConnell 1993; Oranskey et al. 1993). In the case of farmers, pesticide exposure is the result of occupational hazard via spraying of chemicals in the fields which may cause cutaneous and respiratory route absorption predominantly leading to non-Hodgkin's lymphoma (Hoar et al. 1986).

5.4 Different Types of Green Materials Which Can Be Used for Removal of Pesticides

Seeing the impact of the pesticide on environment, human health and our ecosystem, the need of the day is to use green materials for removing pesticides. These green materials are economic and readily available and may be regenerated after use without imposing pollution issues. The most easily affected source of pesticide contamination is water which directly or indirectly affects our ecosystem. The major health-related issues are caused mainly by water contamination. As per the literature survey, various green materials have been reported which can be used for removal of pesticides like:

1. Carbonaceous adsorbents
2. Agricultural waste adsorbents
3. Industrial waste adsorbents
4. Inorganic material adsorbents
5. Polymeric adsorbents
6. Bioadsorbent
7. Nanomaterial-based adsorbents

5.4.1 Carbonaceous Adsorbents

The surface phenomenon which is dependent on the available number of porous sites, different types of interactions and specific surface area of adsorbent is well known as adsorption. The main adsorbent considered is carbonaceous material competent to adsorb a range of organic chemicals. Activated carbon has the property of high porosity and surface area making it efficient to remove different varieties of pesticides from wastewater. Carbonaceous adsorbents are considered as a versatile material for several technological process applications. The different kinds of activated carbon resources are in use, such as granular activated carbon (GAC) (Domingues et al. 2005; Kim et al. 2008; Sotelo et al. 2002a, b; Kitous et al. 2009), powdered activated carbon (PAC) (Kouras et al. 1998; Hu et al. 1998; Matsui et al. 2002; Fernndez-Prez et al. 2005; Sarkar et al. 2007; Ohnoa et al. 2008), carbon cloth (Ayranci and Hoda 2004; Lopez-ramon et al. 2007), carbon fibres (Lopez-ramon et al. 2007; Faur et al. 2005; Martian-Gulloan and Font 2001; Cougnaud et al. 2005), black carbon (Qiu et al. 2009), activated carbon composites (Castro et al. 2009) and commercial activated carbon (CAC) (Ayranci and Hoda 2004; Ayranci and Hoda 2005; Hamadi et al. 2004) (Fig. 5.1). Among these, GAC and PAC forms of activated carbon are most used because of their effective adsorption capability in a wide variety of pesticides (Kyriakopoulos and Doulia 2006). Recently, many researchers have made an attempt to produce activated carbons from renewable and cheaper precursors for removal of a variety of pollutants, especially industrial and agricultural by-products. Few of the carbons are primed from biomass and wastes like date stone (Danish et al. 2010; Hameed et al. 2009), wood (Sudhakar and Dikshit 2008), biochar (Cao et al. 2009), coconut shell (Sharma et al. 2008; Igntowicz 2009), coconut fibres (Sharma et al. 2008), bagasse (Sharma et al. 2008), Sal wood (Sharma et al. 2008; Mishra and Patel 2008), green waste (Zheng et al. 2010), peat moss (Aroguz 2006), horseshoe sea crab shell (Gulen et al. 2005), corn stillage (Tsui and Roy 2008) and oil palm fronds (Salman and Hameed 2010a, b).

Mohammad (2013) reported the role of activated carbon generated from apricot stone as an ethoprophos pesticide adsorbent based on function of pesticide concentration, adsorbent dose, temperature and contact time. The adsorbent's sorption competence was analysed by Langmuir equation as 20.04 mg/g. The pseudo-second-order kinetic model described the data in the best possible way. Chang et al. (2011) demonstrated the efficiency and viability of low-cost adsorbent of rice straw activated carbon for removal of carbofuran from wastewater. The carbofuran pesticide showed increased adsorption capacity with concentration and decreased adsorption capacity due to increase in pH and temperature. Njoku et al. (2014) showed activated carbon from sky fruit husk (SFH) as potential adsorbent with large active surface area for the elimination of bentazone herbicide. Freundlich isotherm studies were well fitted to indicate heterogeneous surface structure. The bentazone adsorbed by SFHAC decreased with increase in pH of the solution.

The biosorption potential of corncob, sugar beet pulp, vermiculite, corncob char, perlite and sediment for efficient removal of glyphosate, 3,4-dichloroaniline

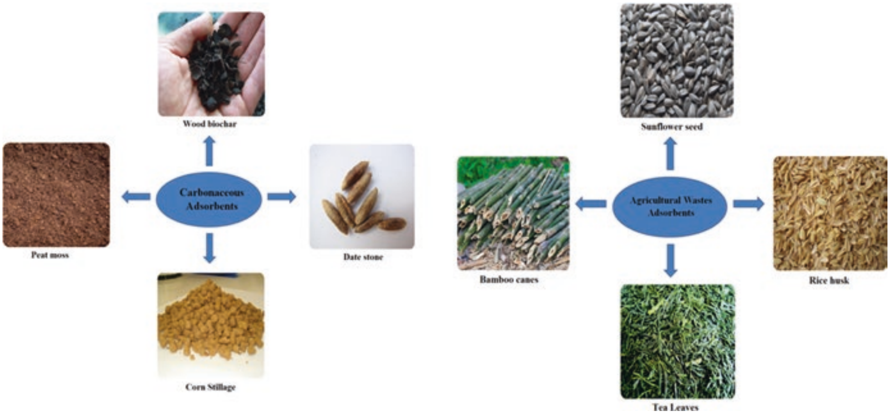

Fig. 5.1 Different sources of carbonaceous adsorbents and agriculture waste adsorbents

(3,4-DCA) and diuron was tested by Huguenot et al. (2010). The result showed that no preliminary treatment was required by sand and sugar beet pulp for the removal of diuron and 3,4-DCA and may retain 50% of the pollutant at the given concentration level. Ioannidou et al. (2010) studied the effectiveness of activated carbon carbon generated from kernel, soya stalks, olive corncob and rape seed stalks for the adsorption of acaricide bromopropylate.

5.4.2 Agricultural Waste Adsorbents

The by-products and waste materials from the industries and agriculture are the resource of low-cost adsorbents because of their abundance and low processing requirement. Recently, lignocellulosic materials have been extensively studied as agriculture waste adsorbent due to their easy availability, biodegradability and low cost. They have been reported to quantitatively accumulate various organic compounds like dyes, bromate and pesticides and heavy metals (Ahmad et al. 2007, 2009a, b; Akhtar et al. 2007; Memon et al. 2007; Rafatullah et al. 2009; Ibrahim et al. 2010; Sulaiman et al. 2010; Danish et al. 2010; Dulman and Cucu-Man 2009; Febrianto et al. 2009; Nanseu-Njiki et al. 2010). The agriculture waste adsorbents are abundant in polysaccharides (cellulose and hemicelluloses) and lignin constituting hydroxyl and carboxyl groups (Fig. 5.1). The pesticides interact with these functional groups on agricultural adsorbents and help in 90% adsorption (Ofomaja 2008). In order to enhance the competence of these materials, the functionalization of the material was carried out by grafting organic molecules with active groups. The application of hybrid materials in treatment technology resulted in adsorbent leading to significant increase in adsorption capacity compared to raw materials (Hsu and Pan 2007; Said et al. 2009). Several latest publications accounted the application of low-cost and locally accessible adsorbents, e.g. ayous sawdust (Witczak and Abdel-Gawad 2014), rice husk (Hsu and Pan 2007), date stones (El Bakouri et al. 2009), watermelon peels (Memon et al. 2008), rice bran (Akhtar et al. 2007), pine sawdust (Rodriguez-Cruz et al. 2008), oak sawdust (Rodriguez-Cruz et al. 2008), tea leaves (Islam et al. 2009), wood sawdust (Boussahel et al. 2009), mango kernel (Memon et al. 2009), peanut shells (El Bakouri et al. 2008), sunflower seed shells (Rojas et al. 2014), chestnut shells (Memon et al. 2007) and bamboo canes (El Bakouri et al. 2008).

It was reported that ayous sawdust was capable to quantitatively adsorb paraquat at a higher rate due to the pseudo-second-order kinetics where pH has a remarkable effect on the reaction (Nanseu-Njiki et al. 2010). Nanseu Memon et al. (2008) demonstrated methyl parathion adsorption from wastewater by means of watermelon peels which were chemically and thermally treated as a low-cost adsorbent. Rodriguez-Cruz et al. (2008) analysed the consequence of different wood pretreatments on the sorption–desorption of metalaxyl and linuron by woods. The data showed that wood residues are low-cost and environmentally friendly matter capable of removing pesticides from soils. The absorption of pesticides was higher by pine than by oak because of high lignin content in pine.

In a report, the removal of endosulfan in biological denitrification reactor (upflow) with wheat straw as a source of carbon showed a high efficiency of removal for endosulfan (α + β) (Aslan and Turkman 2004). Rojas et al. (2014) utilized rice husk, sunflower seed shells, composted sewage sludge and soil as adsorbent for removal of endosulfan sulphate, alachlor, atrazine and trifluralin molecules from water.

5.4.3 Industrial Waste Adsorbents

Industrial wastes like fly ash, sludge and slurry of carbon are defined as low-cost materials due to their local availability and used as potential adsorbents for pesticide treatment. The solid waste generated from lignite coal-fired thermal power station is fly ash which is considered as a low-cost adsorbent with significant adsorption capacity for organic chemicals (Wang and Wu 2006). Some reports have shown characteristic sorption potential of fly ash (Majumdar and Singh 2007; Singh 2009) and have suggested its use in the removal of pesticides from wastewater samples (Sharma et al. 2008) (Fig. 5.2). The coal fly ash has high retention capacity for metribuzin, metolachlor and atrazine (Singh 2009). The maximum absorbed pesticide was atrazine and then metolachlor and metribuzin. The absorption efficiency of herbicide on fly ash was dependant on its initial concentration, and highest removal of herbicide was shown at lower concentrations.

The washed-out and acid-activated bleaching earth may be exploited as a potential adsorbent for MCPA removal from wastewater effluent. The wastes from industries like carbon slurry from fertilizer industry and blast furnace slag and dust and sludge from steel industry waste may be used for removal of carbofuran and 2,4-D from aqueous solution. The adsorbent prepared from carbonaceous material of carbon slurry showed adsorption capacity of 212 and 201 mg g^{-1} for 2,4-D and carbofuran at 25 °C and pH 7.5 (Srivastava et al. 2009). Sharma et al. (2008) demonstrated in his paper the use of different adsorbents for removal of atrazine from water at 0.05 and 0.1 ppm levels.

5.4.4 Inorganic Material Adsorbents

The clay minerals are natural and well-known source of adsorption due to their abundance, low cost, high sorption properties and capacity for ion exchange. Besides these, they have layered structure and are considered a good host for the adsorbates. The clay mineral such as clinoptilolite, montmorillonite, eluthrilithe, cloisite, faujasite, kerolite and palygorskite has emerged as a major adsorbent for inorganic ions and organic molecules. The use of organo-clay complex adsorbents as a substitute to activated carbon is also investigated. They have been often used in industrial processes as adsorbents for the control of organic contaminants from

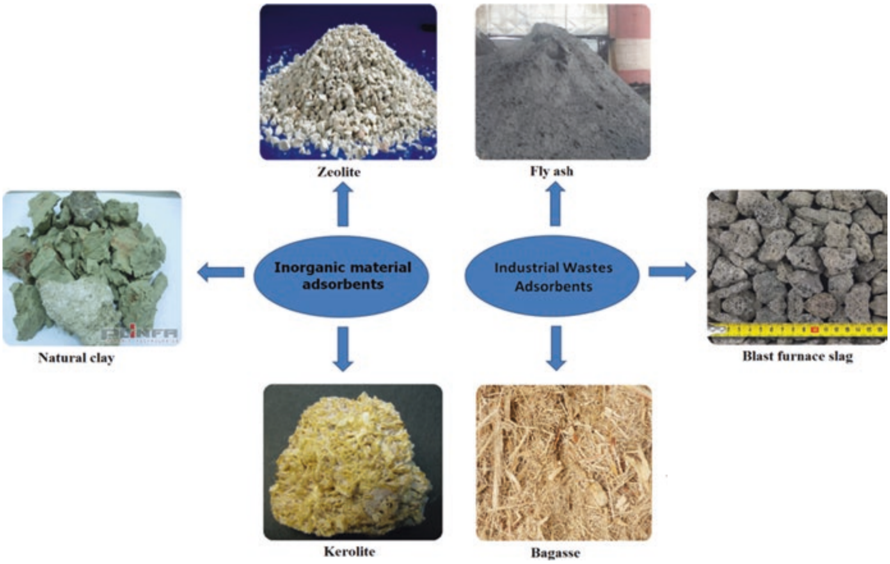

Fig. 5.2 Different sources of inorganic material adsorbents and industrial waste adsorbents

industry (Sanchez-Martin et al. 2006; Suciua and Capri 2009), for the pesticide treatment from water (Cruz-Guzman et al. 2005), for the development of slow-release pesticide formulations (Carrizosa et al. 2000) or for the examination of bioavailable potential (Singh et al. 2003) and photostabilization of sorbed pesticides (Margulis et al. 1992) (Fig. 5.2).

Zeolites are crystalline, microporous aluminosilicates of natural or synthetic origin. They are inorganic polymer of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral molecules. A pure solid framework of silica (SiO_2) is not charged, but some of the Si^{4+} in the silica is replaced by Al^{3+}, thus making the framework negatively charged (Payra and Dutta 2003). Flanigen (2001) classified zeolites based on the ratio of Si/Al as low-silica/hydrophilic zeolites (Si/Al 1–1.5), intermediate silica/intermediate hydrophobic (Si/Al 2–5) and high-silica/hydrophobic zeolites (Si/Al > 10). The hydrophilic property of zeolite increases with aluminium content in the zeolite framework and vice versa (Cekova et al. 2006). The ratio of Si/Al is an important characteristic of zeolites. The differences in the ratio of Si/Al may result in variations in distribution of negative charge density in the structural frameworks, pores of different diameters, the absence of hydration water or other ligands and the presence of extra-framework cation (Munthali et al. 2014).

Pavlovic et al. (2005) deliberated the adsorption of pesticides picloram, 2, 4-D and clopyralid, which are acidic in nature, on calcined hydrotalcite. The sorption takes place through the reformation of the layered structure with the anionic species (pesticide) located as a monolayer in the interlayer and/or on the external surface and edges of the hydrotalcite particles. Urena-Amate et al. (2008) studied the adsorption property of modified kerolite-rich materials for chloridazon from water. The batch experiments data showed that the treatment of kerolite at 600 °C was efficient in removing chloridazon from water. Suciu and Capri (2009) studied the competence of various clay samples and modified ones in eradicating pesticide residues at low concentrations. The adsorption property of the montmorillonite clay and two micelle–clay complexes for pesticides was analysed to adsorb the maximum amount of pesticide to attain a dose–effect relationship.

Ibrahim and Jbara (2009) demonstrated the use of faujasite, a mineral group in the zeolite family, in the removal of paraquat which showed an efficiency of 59% without thermal activation, whereas their efficiency was enhanced to 71% at 200 °C thermal activation. This removal of paraquat from wastewater increased from 93% to 99.5% using that thermally activated faujasite forms at 200 °C and 300 °C. Valickova et al. (2013) investigated the use of zeolite for removal of chlorinated pesticides, with highest removal efficiency (93.8%) for hexachlorobenzene during observed contact time. The next highest removal efficiency (92.1%) was observed for heptachlor, followed by hexachlorobutadiene (83.7%), pentachlorobenzene (72.9%) and lindane with 25.8%. Arnnok and Burakham (2014) verified the better efficiency of modified sorbents in removal of carbamate pesticides in aqueous solutions. It was observed that cetyltrimethylammonium bromide-modified zeolite showed high adsorption rate for carbamate pesticides due to the hydrophobicity of surfactant aggregate on solid surfaces. The adsorption percentages of carbofuran, oxamyl, carbaryl, carbosulfan and methiocarb were found to be above 94%. De Smedt et al. (2015) evaluated that properties like polarity and mobility of the pesticides influenced the adsorption rate. The static pesticides like isoproturon, metalaxyl-m and imidacloprid have the tendency to be associated with zeolite, whereas pesticides like bentazon and clopyralid which are mobile pesticides are partitioned more in water. Both non-ionic pesticides such as metalaxyl-m and isoproturon have strong likeness for zeolites based on their polar nature.

5.4.5 Polymeric Adsorbents

An emerging alternative for adsorbents is polymeric material with their wide surface area, adaptable surface chemistry, ideal mechanical rigidity and viable regeneration ability under meek conditions. The polymeric adsorbents effectively entrap organic pollutants like phenolic compounds, aromatic or polyaromatic hydrocarbons, organic acids and derivatives of alkanes. In 1974, Richard and Fritz (1974) researched dieldrin in river water (in ppb) which was recovered on a column of polymeric resin by sorption, consequently followed by elution with acetonitrile. The adsorption ability of simazine, chlorotoluron, isoproturon, atrazine and diuron pesticides onto Chemviron F-400 and Hypersol-Macronet™ polymer was compared by Streat et al. (1998).

The adsorption of diuron 2-aminonaphthalene-1-sulfonate and 1-naphthol onto polymeric resin styrene divinylbenzene copolymer or polyvinyl benzene was investigated by Frimmel et al. (1999). Koskinen et al. (1999) also used resin along with solvents water and methanol to test adsorption rates of pesticides such as alachlor, imidacloprid, atrazine, isofenphos, triadimefon and nicosulfuron. Yoshizuka et al. (2000) synthesized chitosan polymer-based silver-complexes (SCMs) with glutaraldehyde and epichlorohydrin as cross-linking agent and used for removal of methyl parathion. The results showed that glutaraldehyde-cross-linked SCM provided good reusability in adsorption and release experiments of methyl parathion.

Later on, the adsorption capability of polymeric resins [Amberlite XAD-4 (polystyrene-divinylbenzene copolymer) and XAD-7 (non-ionic aliphatic acrylic polymer)] for the adsorption of herbicides amitrole, alachlor, prometryn and trifluralin from water was studied. The adsorption isotherm approach of Langmuir or the Freundlich isotherm model was characterized by temperature- and pH-dependent equilibrium constants (Kyriakopoulos et al. 2003; Kyriakopoulos et al. 2005). Trochimczuk et al. (2003) synthesized a series of six copolymers of acrylonitrile (AN)/divinylbenzene (DVB) and methacrylonitrile (MAN)/DVB by suspension polymerization which had inherent property of being porous. They showed excellent sorption behaviour of pesticides and herbicides on these highly polar polymeric sorbents. It was found that AN and MAN showed sorption of atrazine, imazapyr and 2, 4-dichlorophenoxyacetic acid depending upon the hydrophilicity of these pesticides. Macronet MN-150 and MN-500 as hyper-cross-linked polymers were studied for removal of methomyl pesticide from aqueous solution (Chang et al. 2008), and polymer MN-150 had a high potential as an adsorbent when compared to MN-500.

To enhance the adsorption performance of the polymeric adsorbents towards several other pollutants like sulfonated pollutants which are highly water-soluble compounds and heavy metals ions, functionalization and surface modification may prove to be an efficient approach (Naushad et al. 2015). As far as literature survey is concerned, the report of research work on adsorption of pesticides from aqueous solution by polymeric resin is very limited. Among the polymeric resins' category, Amberlite adsorbents are widely used for the removal of pharmaceuticals, pesticides and organic compounds from aqueous solutions (Ahmad et al. 2010; Naushad et al. 2013). In 2007, Liyan et al. (2007, 2008) innovated biomimetic fat cell (BFC) which was synthesized by interfacial polymerization as an agent for removal of lindane. BFC has a hydrophilic membrane of polyamide and a hydrophobic nucleolus of triolein which may accumulate hydrocarbons. The characteristics adsorption was observed by a novel adsorbent material, poly(acrylamide) and methylcellulose (PAAm-MC) hydrogel for the removal of paraquat from water (Aouada et al. 2009). The MC in PAAm chains forced changes in morphology, hydrophilicity and adsorption properties of the hydrogel and influenced adsorption capacity of hydrogel. The hydrogel with 6.0% AAm with 0.75% MC reported highest adsorption capacity (qeq = 14.3 mg/g) and gets swollen in 45.7 mg/L of paraquat solution.

Alila and Boufi (2009) in their report demonstrated the use of several tailored cellulose fibres and their competence for the elimination of various aromatic organic compounds including herbicides like alachlor, atrazine and linuron. The cellulose fibres are chemically modified by grafting hydrocarbon chains with different organic moieties which give hydrophobic reservoirs for accumulation of organic compounds.

5.4.6 Bioadsorbents

Biosorption is phenomenon which is independent of metabolism (chemical and physical adsorption, ion exchange, electrostatic interaction, chelation, complexation and micro-precipitation) and takes place in the cell wall. The main characteristics of biosorption are high efficiency and selectivity, low economic value and good performance. Seaweeds are used as biosorbents and show performances equivalent to ion-exchange resins. The biomass is employed to eradicate pesticides, but the sustenance of biomass during adsorption process is hard due to continuous requirement of nutrients. Table 5.1 shows various natural adsorbents for the removal of different pesticides with removal efficiency from aqueous solutions. Bell and Tsezos (1987) studied the pentachlorophenol (PCP) biosorption via two kinds of microbial biomass (inactive): a mixed culture of aerobic activated sludge and a pure culture of *Rhizopus arrhizus*. It was reported that the dead cells of *Rhizopus arrhizus* had a superior capacity for biosorption for PCP as compared to dead activated sludge. The dead microbial cells are also used in biosorption and water treatment since they are least affected by toxic materials and do not require nutrients and can be recycled several times. The dead microbial cells can be stored for a long time without putrefaction at room temperature. The inactivated biomass binds pollutants depending on the species, size, ionic charge, type of biomass, surface properties and environmental conditions (Aksu 2005). The metabolization capability of microorganisms to certain pesticides has attracted attention because of environmental perseverance and toxic effect of these chemicals. In few cases, contaminant metabolism by microbes may generate toxic metabolites, whereas many aerobic bacteria and fungi such as *Pseudomonas pickettii*, *Alcaligenes eutrophus*, *Desulfomonile tiedjei* and *Phanerochaete chrysosporium* utilize organic pesticides as the energy source (Gupta et al. 2002; Aksu and Kabasakal 2004). Ghosh et al. (2009) analysed the adsorption performance of *Rhizopus oryzae* biomass for lindane. It was found that the adsorption phenomenon was dependant on hydrophobic interaction rather than solution pH or incubation temperature.

Chatterjee et al. (2010) deliberated the interaction between an organophosphorus pesticide (malathion) and biomass of *Rhizopus oryzae*. They studied that the amino groups of chitosan cause chemical interaction between malathion and *Rhizopus oryzae* cell wall. Shankar et al. (2018) reported the advancement of a bioadsorbent with improved adsorption properties for removal of pentachlorophenol (PCP) from aqueous solutions. A modified chitosan CHTA was obtained by cross-linking chitosan (CHT) with 2-hydroxy-1-naphthaldehyde, and further modification was done by grafting with $CuCl_2$ to prepare CHTAC. The highest adsorption capacity was shown by CHTA (39.1 mg/g) followed by CHTAC (35.4 mg/g) and CHT (24.4 mg/g) at room temperature and neutral pH. The rate of adsorption followed a pseudo-second-order model on all the three materials. Bakka et al. (2018) showed the adsorption activities of aldrin insecticide on treated patellidae shells (TPS) from water by batch method. The maximum biosorption capacity after 50 min of contact time was about 111.63 mg/g (with 30 mg/L of pesticide and 25 mg of biosorbent). The data from

Table 5.1 Various natural adsorbents for the removal of different pesticides (removal efficiency) from aqueous solutions

S. no	Natural adsorbent	Pesticide removed	Removal efficiency	References
1	Indian soils	Triazophos	90%	Fuller and Sudha (2015)
2.	Alluvial soil	Imidacloprid	95%	Bajeer et al. (2012)
3.	Local clay	Carbaryl	97–99%	Quardi et al. (2013)
4.	Natural clay	Methomyl	27.6–32.9%	El-Geundi et al. (2012)
5.	Silt loamy	Imidacloprid	77%	Abbas and Al-Madhhachi (2015)
6.	Sandy soil	Imidacloprid	93.2%	Abbas and Al- Madhhachi (2015)
7.	Silt loamy	Pirimicarb	86.2%	Abbas and Al- Madhhachi (2015)
8.	Sandy soil	Pirimicarb	99.7	Abbas and Al- Madhhachi (2015)
9.	Watermelon peel	Pirimicarb	98.2%	Fuller and Sudha Chaithanya (2015)
10.	Watermelon peel	Imidacloprid	95.4%	Fuller and Sudha Chaithanya (2015)
11.	Used tea leaves	Pirimicarb	92.8%	Fuller and Sudha Chaithanya (2015)
12.	Used tea leaves	Imidacloprid	90.3%	Fuller and Sudha Chaithanya (2015)
13.	Acacia etbaica	Aldrin, dieldrin, DDT	95–99%	Fuller and Sudha Chaithanya (2015)
14.	Vermicompost	Methyl parathion	90–95%	Mendes et al. (2012)
15.	Rice straw	Carbofuran	29.6%	Fuller and Sudha (2015)
16.	Pine bark	Lindane	80%	Fuller and Sudha (2015)
17.	Mango kernels	Methyl parathion	98%	Memon et al. (2009)

(continued)

Table 5.1 (continued)

S. no	Natural adsorbent	Pesticide removed	Removal efficiency	References
18.	Rice husk	2,4-Dichlorophenoxyacetic acid	90%	Hsu and Pan (2007)
19.	Rice husk ash	Metolachlor, alachlor, fipronil, chlorpyrifos, β-endosulfan, α-endosulfan	90%	Saha et al. (2014)
20.	Orange peel	Carbofuran	84.49 mg/g	Chen et al. (2012)
21.	Banana stalks	Carbofuran	96.97–97.35%	Salman and Hameed (2010)
22.	Walnut shells	Carbofuran	97–99%	Memona et al. (2014)
		Chlorpyrifos		
23.	Banana peel	Atrazine	>90%	Claudineia et al. (2013)
		Ametryne		
24.	Pomegranate peel	Oxamyl	80–90%	Mohammad et al. (2013)
25.	Coconut shell charcoal	Atrazine	92.4%–95.2%	Sharma et al. (2008)
26.	Bagasse	Atrazine	76.5–84.6	Sharma et al. (2008)
27.	Patellidae shells	Aldrin	91.72%	Bakka et al. (2018)
28.	Wood charcoal	Atrazine	95.5%	Alam et al.(2000)
29.	Sunflower seed shells	Atrazine	73.9%	Rojas et al. (2014)
		Alachlor		
		Endosulfan		

thermodynamic study demonstrated that the biosorption of aldrin on TPS was spontaneous, exothermic and highly favourable. Table 5.2 shows different low-cost adsorbents generated from waste products for treatment of pesticides in contaminated water.

5.4.7 Nanomaterial-Based Adsorbents

Nanomaterial-based adsorbents are the new trend in the treatment of contaminated water. Nanoparticles have proved to be an excellent adsorbent due to their small size, catalytic potential, high reactivity, ease of separation, large number of active sites and large surface area for interaction with different pollutants (Ali 2012). An effective adsorbent was developed for the first time from graphene-based magnetic nanocomposite for the five carbamate pesticides, viz. carbofuran, diethofencarb, isoprocarb, metolcarb and pirimicarb, in environmental water samples before high-performance liquid chromatography-diode array detection (Wu et al. 2011). Studied

Table 5.2 Different low-cost adsorbents generated from waste products for treatment of pesticides in contaminated water

Household waste	Agriculture product	Industrial waste	Sea materials	Soil and ore materials	References
Fruit waste	Bark and other tannin-rich material	Fertilizer wastes	Chitosan and seafood processing wastes	Clays	Ali et al. (2012)
Coconut shell	Sawdust and other wood-type materials	Sugar industry wastes	Seaweed and algae	Red mud	
Scrap tyres	Rice husk	Petroleum wastes	Peat moss	Zeolites	
	Other agricultural waste		Miscellaneous waste	Sediment and soil	
				Ore minerals	

the efficiency of a polymer matrix nanocomposite of polystyrene and Fe_3O_4 nanofillers by in situ polymerization method to remove organochlorine pesticides. The nanocomposites showed lesser uptake of endrin, lindane and aldrin pesticides in batch experiment, and the estimated adsorption capacity of polymer nanocomposites was low as compared to other alternatives.

Rahmanifar and Moradi Dehagh (2013) synthesized composite of chitosan–AgO nanoparticles (CS–AgONPs) for permethrin pesticide removal from water. The CS–AgONPs polycomposite was optimized with initial concentration of pesticide, amount of sorbent, agitating time and pH parameters to remove permethrin. The CS–AgONPs beads may recover 99% of permethrin at room temperature and pH 7, which was characterized by UV spectrophotometer at 272 nm. Moradi et al. (2014) synthesized bionanocomposite chitosan–ZnO nanoparticles (CS–ZnONPs) beads for removal of permethrin pesticide from aqueous media. The results ensured that bionanocomposite (0.5 g at room temperature and pH 7) may remove 99% of permethrin (25 mL, 0.1 mg L^{-1}) at 272 nm. Further, the chitosan–zinc oxide nanoparticle composite adsorbent was used in the online column for pesticide removal, and the regeneration of column was done with NaOH solution (0.1 M) for reuse. The CS–ZnONPs composite beads are regarded as new promising composite material for water treatment with 56% regeneration after three consecutive cycles. Yousefi (2017) investigated the synthesis of carbon nanoparticles from pomegranate for the removal of pesticides like glyphosate, trifluralin and 2,4-dichlorophenoxyacetic acid from water. The nanomaterial provided high surface area, faster uptake kinetics and more capacity. Several physico-chemical parameters like pH, adsorbent dosage initial concentration and equilibrium contact time were analysed. The results confirmed that removal of pesticides glyphosate, 2,4D and trifluralin from water depended on pH and their removal efficiency observed at pH 9 was 92.6, 78 and 92%, respectively.

Moreover, a new class of nanomaterials used is carbon nanotubes (CNTs) composed of graphite carbons with single or many concentric tubules. CNTs are of two types: single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs). CNTs have good potential to remove a wide range of pesticides because of porous structure and the presence of surface functional groups that undergo chemical or thermal modifications to improve the performance. The adsorption capability of CNTs for organic chemicals may involve hydrophobic effect, π-π interactions, covalent bonding, hydrogen bonding and electrostatic interactions. The organic molecules with benzene ring or double bond, polycyclic aromatic hydrocarbons (PAHs) and polar aromatic compounds adsorb on the surface of CNT via π-π interaction. In 2008, Yan et al. (2008) examined the adsorption and desorption property of carbon nanotubes for pesticide atrazine in batch reactors. The adsorption capacity of SMWNT20 and r-MWNT was compared by surface area, and it was inferred that besides surface area, there are other factors like surface chemistry as well which may determine the adsorption capacity. The reversible adsorption on CNTs of atrazine was due to external surface adsorption and no closed interstitial spaces. The diuron adsorption onto MWCNTs showed oxidation treatment of MWCNTs giving rise to high pore volume, surface area and an increase in adsorption capacity. Moreover, the reaction was spontaneous and exothermic (Deng et al. 2012). SWCNTs demonstrated higher adsorption capacity for a phenoxy acid herbicide, 4-chloro-2-methylphenoxyacetic acid (MCPA) than MWCNTs with different nanoscale metal oxides, viz. Al_2O_3, TiO_2 and ZnO. The adsorption kinetics followed pseudo-second-order kinetics, and the adsorption phenomenon was exothermic and spontaneous (De Martino et al. 2012). The dichlobenil and diuron adsorption by MWNTs has been extensively studied, and it was established that the adsorption increased with increasing pore volume and surface area of MWNTs. The adsorbed amount and surface coverage of diuron were more than dichlobenil which may be due to larger van der Waals interaction of diuron than dichlobenil. The surfactant-dispersed SWNTs and MWNTs demonstrated inhibited adsorption of atrazine. The cationic (cetyltrimethylammonium bromide, CTAB) and anionic (sodium dodecylbenzenesulfonate, SDBS) surfactants have inhibitory effects on the adsorption property of MWNTs, although the inhibitory effect of SDBS on SWNTs was slightly more than that of CTAB (Taghizade Firozjaee et al. 2018). Keshvardoostchokami et al. (2018) synthesized nanocomposite of silver–graphene oxide and studied its application as an adsorbent for imidacloprid from aqueous medium in batch experiment. Several parameters were optimized like time, pH, concentration of pesticide, adsorbent dosage, etc. The results based on experiments indicated the removal of 63% of the pesticide by 0.03 g of the adsorbent from 50 mL water with 10 mg/L of imidacloprid at pH = 6.6 after 60 min contact time in optimum conditions. The adsorption processes followed kinetics and isotherm for Freundlich and pseudo-second-order models.

5.5 Conclusion

The review presents the efficient and economic role of nonconventional adsorbents in water treatment and waste management. The pesticide contamination of water resources has evolved as a vital environmental concern with respect to the long-term and low-dose effects of pesticides on public health and aquatic lives. The excessive use of pesticides in agriculture has led to ground- and surface water contamination, and its consumption has adverse ecotoxicological effects on human health, aquatic flora and fauna. Seeing the impact of the pesticide on environment, human health and our ecosystem, the need of the day is to use green materials for removing pesticides. These green materials are economic and readily available and may be regenerated after use without imposing pollution issues. The major health-related issues are caused mainly by water contamination. Various green materials in the form of adsorbents have been reported which may be applied to removal of pesticides from wastewater like carbonaceous, agricultural wastes, industrial wastes, polymeric adsorbents, bioadsorbent, inorganic material and nanomaterial-based adsorbents. In the future the use of these green materials will gain much momentum due to high economic state and regeneration ability.

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Chapter 6
Rice Husk Derived Adsorbents for Water Purification

S. K. Shukla

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Abstract Rice husk (RH) is an abundantly available, inexpensive agro waste with several industrially important chemicals and properties, such as composition, surface adsorption, strength, bulk density, calorific values, abrasion, etc. Therefore, it has been widely modified and used in different applications, including fuel for boilers, fillers in rubbers, fodder for animals, and a source of different materials, such as silica, silica carbide, cellulose, carbon nanotubes, and graphene. The porosity and adsorption of RH and its derived adsorbents have been explored in water purification. The effectiveness of water purification is based on morphology, structure, chemical composition, and surface area, which attracts scientists for innovation. Some of the RH derived materials explored for water purification are biochar, activated carbon, silica, and hydrogels, along with their merits and demerits. In the light of the above developments, the present chapter describes the RH as a source of adsorbent and its application in the removal of various pollutants from drinking water and wastewater. The properties and various methods used on RH to convert it into adsorbents are also discussed. The reported literature indicates that RH has

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S. K. Shukla (✉)
Department of Polymer Sciences, Bhaskaracharya College of Applied Sciences,
University of Delhi, Delhi, India

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enormous potential for water purification but several limitations need to be addressed. The hurdles and success story of the conversion and application of RH in water purification have been represented along with future challenges.

Keywords Rice husk · Chemical treatments · Adsorbents · Water purifications · Biofilters

6.1 Introduction

Exponential increments of pollutants in natural and artificial water bodies have alarmed society and spurred the design of elimination and control mechanisms. The pollution of water has occurred by natural and anthropogenic sources. Ultimately, we can only control the anthopogenic activities, but natural activities will still continues to pollute the water bodies. Thus, to optimize the level of water pollution, the elimination of pollutants is the only suitable path to save the water bodies (Kumar et al. 2015). Therefore, several adsorbents, such as charcoal, zeolite, nanocomposites, and metal oxides and their hybrids, are explored for removal of water pollutants (Greenstone and Hanna 2014; Haffhold 2011; Nabi and Naushad 2008). However, depletion of natural resources is compelling the development of cost effective materials for water purification applications. In this context, several agro-based biomasses, such as coconut shell, guar gum, peels of different fruits, and rice husk, are explored. Among these biomasses, rice husk (RH) has the advantage of huge perennial production in most parts of the world at a cheap rate (Bhatnagar et al. 2015; Naushad et al. 2016).

Generally, RH is a by-product of the rice milling industry, which is around 20% of the total paddy crop. It is reported that the annual production of paddy is about 500 million tons in developing countries, which yields approximately 100 million tones of RH on a regular basis. Chemically, RH is composed of 94.99% organic compounds and 5% inorganic compounds. The main organic compounds are cellulose, hemicelluloses, and lignin, and the inorganic part is mainly silica along with some trace metals and oxides. Both organic and inorganic compounds bear their own significance in water purification. Thus, RH has been converted into several adsorbents, such as activated carbon, biochar, silica, composite, and hydrogel, for water purification (Soltani et al. 2015 and Liu et al. 2016). The chemical and physical treatments of RH also yield a hybrid matrix containing metals along with a porous and flexible polymeric chain, which provides additional advantages, including high adsorption capacity, photo catalysis, and reactive oxygen species. The significance of the area is also supported by an exponential increase in publication trends (Fig. 6.1).

In the light of the above development, the present chapter introduces the basics of RH and the technique used to convert RH into different adsorbents. The observed advantageous properties of RH-based adsorbents are discussed in comparison to the

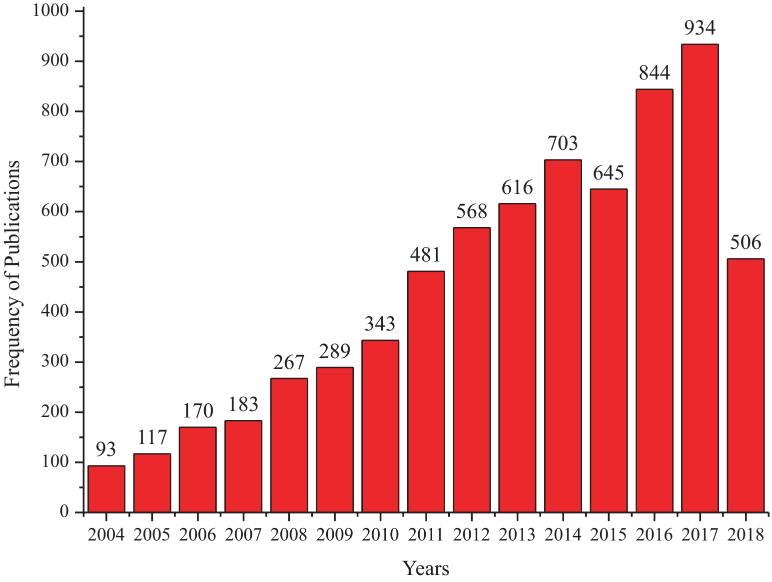

Fig. 6.1 Trends in publication frequency of RH. (Figure redrawn from the data source available by scopus.com, accessed on 15.6.2018; term rice husk)

routine adsorbents used for water purification. The application of developed RH based adsorbents has also been described for removal of heavy metals, dyes, pesticides, and microbes, along with their limitations.

6.2 Properties

The basic important properties of RH for different applications are moisture content, bulk density, particle size, heating values, proximate analysis, ultimate analysis, ash composition, and ash fusibility (Table 6.1). The minute properties of RH depend on the variety of paddy, soil compositions, and conditions of cultivations.

Several modifications are also made to modify these properties for suitable applications. For example, chemical modification of RH generates porosity and mechanical strength for making a water filter. A comparison of some RH properties is made for different RH collected from different cultivations sites and a variety of paddies (Mansaray and Ghaly 2007; Zhang et al. 2012). The properties that make RH suitable for water purification are processability, surface area, and catalytic properties. The addition of transition metal oxides such as titanium oxide in RH derived silica has been reported as more suitable for catalytic removal of dyes present in wastewater due to presence of high surface area and porous structure (Yang et al. 2011).

Table 6.1 Properties of rice husk

S.N.	Properties	Values
1	Bulk density	86–114 kg/m^3
2	Moisture contents	8·68–10·44%,
3	Particle size	0.212–0.850 mm
4	Calorific values	3000 K Cal/kg

6.3 Preparation of Adsorbents

RH is a biodegradable composite material with high calorific value, hardness, and high thermal and chemical stability. Thus, simple treatments are unable to convert it into valuable products. Therefore, integrated treatments, such as thermochemical and mechanochemical, are required for development of useful adsorbent. Some of the adsorbents prepared from RH are silica, zeolite, activated carbon, biochar, metal silicate, and hydrogels (Liu et al. 2016). All these adsorbents are explored and bear their own merits and demerits for water purification. A pictorial representation of RH conversion into adsorbents is given in Fig. 6.2.

Silica is a major component of the residual part of RH, and thus several chemical treatments are explored for extraction of silica and its derivatives from RH. Silica present in RH is in gel form, and applied chemical treatments modified the structure of silica present in RH from amorphous to crystalline and powder to aerogel. The size reductions up to nano size are also explored for modification of obtained silica using templates. The additional metals in silica yield different properties, such as magnetism, florescence, and catalytic ability, which bear several advantages for water purification. Feng et al. (2018) prepared silica-based aerogel from rice husk ash by an innovative route. The obtained silica aerogel bears improved specific area and pore volume due to variation in the polymerization degree of SiO_2. The optimal silica shows extremely high specific surface area 945.8 m^2/g, pore volume 0.889 cm^3/g, and low density 0.071 g/cm^3 with uniform pore size distribution and high heat resistance.

Carbonization is an integrated process that transforms carbon containing materials into various forms of carbon. Since RH contains approximately 80% organic compounds, such as cellulose, hemicellulose, lignin, etc., it has been used to develop several carbon forms, including activated carbon, carbon nanotubes, graphene, etc. Activated carbon (AC) is an important adsorbent derived from RH. It has high porosity, high surface area, low bulk density, and is nonhazardous (Kwiatkowski et al. 2012). The basic reaction for preparation of AC is carbonization, which is based on the pyrolysis of RH under different conditions (Masoud et al. 2016 and Chaney et al. 1923). Van and Thi (2014) prepared AC by carbonizing RH at 400 °C under a nitrogen flow of 300 mL min^{-1} for 90 min. The obtained product was impregnated with NaOH in weight ratio of 1/3 followed by thermal treatment. The activated AC shows high surface area and suitability for industrial applications. The obtained AC is also activated by several methods in order to make it more suitable for applications. In modified carbonization processes, the RH has been converted

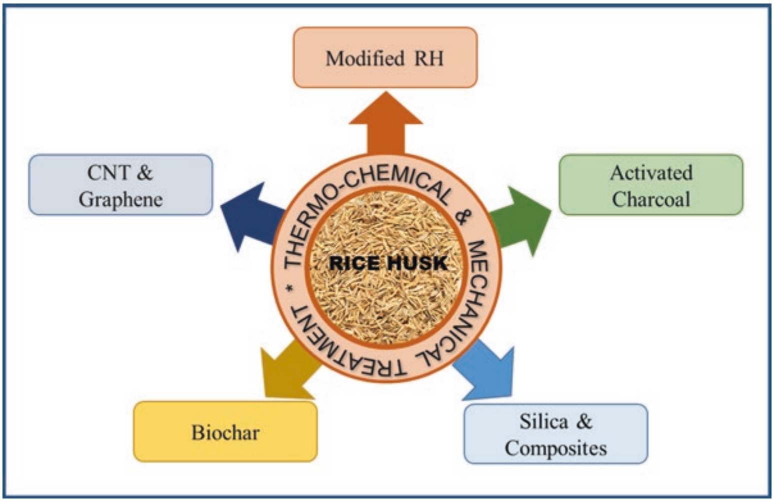

Fig. 6.2 Schematic for development of adsorbents from RH

into carbon nanotube (CNT) and graphene. These are the allotropes of carbon with two dimensional structures along with unique physical, mechanical, electrical, and surface properties.

Biochar (BC) is a form of charcoal, and it is produced with controlled thermal degradation of plant waste, such as wood, rice husk, fruit peels, etc. The RH can be converted into BC after a set of thermo chemical treatments, such as hydrothermal treatments. BC has been prepared by hydrothermal treatment of RH. For example, 5 g of RH was loaded with 30 ml de-ionized water into a 100-ml autoclave and nitrogen gas was used to purge the air outside the reactor. The reactor was held at 573 K for 20 min then cooled to room temperature. The resultant solid products were collected using acetone as biochars for further uses like removal of metal ions (Liu, and Zhang 2009). Sometimes metal oxide has been impregnated in RH derived biochar for improvement in adsorption capacity. The MgO was impregnated in BC by a simple method. The modified composite was found suitable as an effective and eco-friendly adsorbent with enhanced removal of Cd(II) from aqueous solution. It is reported that the adsorption capacities of composite biochar for Cd(II) are enhanced from 6.36 and 18.1 mg/g (Xiang et al. 2018). The change in adsorption is due to an increase in electrostatic interactions owing to the presence of ionic MgO as well as surface complexation capacity due to the presence of the OH group.

Hydrogels are polymeric hybrid structures with efficient sorbent behavior, stretchability, and stability (Zhan et al. 2002). They comprise a three dimensional cross-linked polymer network structure with both hydrophilic and hydrophobic parts, which quickly allow the diffusion of molecules. The presence of different functionalities in hydrogels also controls the different properties, such as catalyst, swelling, and adsorption capacity. It is suitable for a wide range of applications, including water purification. In this regard, several efforts have also been made to develop an RH composite hydrogel along with encapsulating metallic ions, such as iron. The hybrid hydrogel has found effective application for water purification of metal and dyes (Pandey et al. 2017). Jean et al. (2012) prepared poly(acrylamide-*co*-acrylate) with a rice husk ash (RHA) composite hydrogel with optimized swelling properties. The hydrogel was shown to be sensitive to pH and the presence of salts in its surrounding. The composite hydrogels of poly(acrylamide-*co*-acrylate) with RHA bear good characteristics to be applied as soil conditioners for use in agriculture. Similarly, the graft copolymer of RH and polyacrylic-co-acrylamide increased the amide adsorption power up to 869 g/g (Pan et al. 2017).

6.4 Applications

6.4.1 Dyes

Dyes are widely used in different industries, such as textile, rubber, leather, paper, and plastic industries, as coloring agents. However, old machinery and poor processability leads to a significant fraction of dyes remaining unused, which is then drained into affluent industrial water (Gnanasekaran et al. 2018; Ming-Twang et al. 2017). The direct discharge of dye-containing industrial wastewater is increasing pollution levels of water bodies as well as generating secondary toxic chemicals. These chemicals are allergens as well as carcinogenic and mutagenic to organisms at minute concentrations of less than 1 ppm (Ojstrsek and Fakin 2011). These chemicals also enter the food chain through aquatic animals and lead to biomagnifications. Thus, the removal of dyes form water is very important for aquatic organisms as well as water consuming living organisms. Several methods, e.g., chemical oxidation, precipitation, membrane filtration, ion-exchange, adsorption, reverse osmosis, and electrochemical oxidation, have been developed (Pirkarami and Olya 2017). Among the different methods, the adsorption-based water purification is very simple and cost effective. In this regard, several adsorbents, such as carbon nanotubes, metal oxide, silica, polymeric membrane, and hydrogels, are derived from RH (Santhi et al. 2016). RH has also been used as a low cost adsorbent to remove dyes from water samples in direct surface adsorption (Chuah et al. 2005). The catalytic and photo catalytic properties in RH derived materials are also suitably explored for the removal of dyes through catalytic decomposition. The RH derived biochar and silica have been frequently used for this cause. The incorporation of different transition metals generates catalytic behavior for dye removal. In a significant study, mesoporous silica (MCM-48) was prepared from silica gel extracted from rice husk ash and then loaded by nickel oxide (Ni_2O_3) to develop catalytic activity. The MCM-48 played the role of a catalyst support for increasing the photocatalytic properties of nickel oxide. The catalyst was explored for the photocatalytic degradation of Congo red dye under visible light source. The prepared MCM-48 revealed considerable enhancement in the adsorption capacity by 17% and 29% higher than the

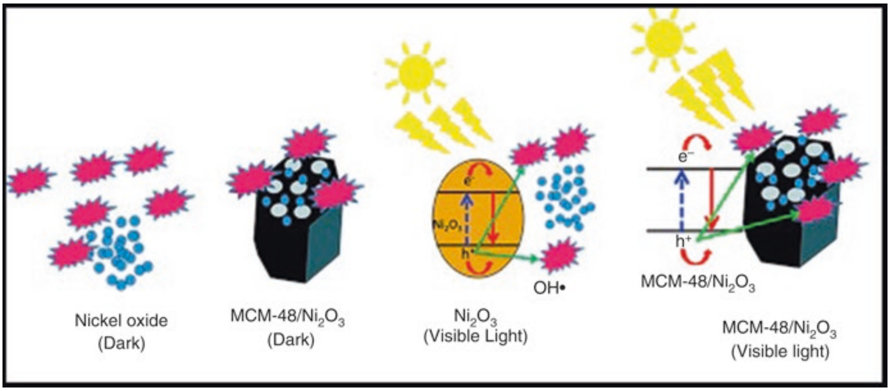

Fig. 6.3 Designing and photocatalytic mechanism of NiO and SiO_2 photocatalysts (Shaban et al. 2017)

adsorption capacity of MCM-48 and Ni_2O_3 (Shaban et al. 2017). The mechanistic approach for synthesis and working catalyst is indicated in Fig. 6.3.

The other technically important and industrially feasible applications of RH derived materials along with their applications in dye removal are given in Table 6.2.

The pH of impure water also needs to be optimized. The effect of pH on adsorption capacity and kinetics has been investigated by Sen and his colleagues. The correlation between pH percentage adsorption and adsorption amount is given in Fig. 6.4, which is an indicator for selection and removal kinetics for designing an experiment for dye removal from water.

6.4.2 *Heavy metals*

The porous, heterogeneous, and metal containing structure of RH is key for it use in removal of heavy metal impurities from water samples (Inyang et al. 2016 and Chuah et al. 2005). Shukla et al. (2014) chemically modified the RH to develop a rice husk-based adsorbent. The developed adsorbent bears better swelling behavior, thermal stability, absorption capacity, and optimized bulk density. The adsorbent was found suitable for effective removal of As(III) at 90% and Cu at 93%. The other adsorbents derived from RHs also have significant application in removal of metal ions from polluted water.

The residual ash of RH, referred to as rice husk ash (RHA), shows porous nature and metal ions adsorption characteristics. The presence of different metal ions makes it suitable for removal of several metal ions, including cadmium (II), nickel (II), and zinc (II) metal ions, from aqueous solutions. Srivastava et al. (2006) developed mesoporous rice husk ash (RHA) as a low cost adsorbent from RH by a set of physicochemical treatments. The obtained RHA had a particle size of 150.47 μm, a BET surface area of 36.44 m^2/g, and an average pore diameter of 42.603 Å. The

Table 6.2 Representative RH derived adsorbents for dye removal

S.N	Adsorbent	Dye	Method	Reference
1	Rice husk	Indigo carmine	Adsorption	Lakshmi et al. (2009)
2	Activated carbon	Acid dye	Adsorption	Mohamed (2004)
3	Activated carbon	Congo red	Adsorption	Sharma et al. (2017)
4	Silica gel composite	Congo red	Catalytic	Shaban et al. (2017)
5	Starch/rice husk ash Composite	Methylene blue	Adsorption	de Azevedo et al. (2017)
6	RHA	Methylene blue	Adsorption	Salem et al. (2018)
7	Chitosan-g-poly(acrylic acid)/RHA composite	Methylene blue	Adsorption	Vaz et al. (2017)
8	Biochar	Malachite green	Adsorption	Leng et al. (2015)
9	Rice husk	Direct blue	Adsorption	Saroj et al. (2015)
10	Rice husk	Methylene blue	Adsorption	Chandrasekhar and Pramada (2006)
11	Rice husk ash	Organic dye	Adsorption	Barbosa et al. (2018)

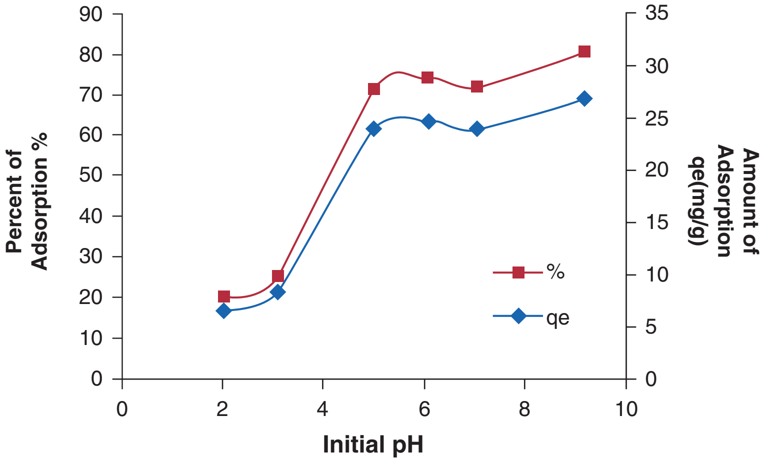

Fig. 6.4 The correlation between pH, removal capacity, and percentage adsorption of dyes (Yagub et al. 2014)

RHA was reported suitable for effective removal of several heavy metals. The other important RH derived adsorbents are compiled in Table 6.3 along with their respective metal removal capacity.

Further, porosity of an adsorbent also depends on the temperature and thermal treatments. In this context, Farhan et al. (2017a, b) thermally treated the RH at higher temperature for adsorbent. The obtained adsorbent was found more suitable for sorption of nickel(II) ions. The temperature and contact time has an important impact on the removal of metal ions.

Table 6.3 RH derived adsorbents for removal of heavy metals

S.N	Adsorbent	Metal ion	Method	Reference
1	Composite of RH	Uranium	Sorption	Youssef et al. (2018)
2	RH-based geopolymer	Cadmium	Adsorption	Maingi et al. (2018)
3	MgO-biochar	Cadminum	Adsorption	Xiang et al. (2018)
4	RH	As	Adsorption	–
5	Biochars	Arsenic and chromium	Adsorption	Agrafioti et al. (2014)
6	Sulfur-functionalized rice husk	Cd(II)	Adsorption	Qu, et al. (2018)
7	Functionalized silica	Cu(II), Cr(III) and Pb(II)	Adsorption	Fatimah et al. (2018a, b)
8	Activated carbon	Cr(VI)	Adsorption	Mullick et al. (2018)
9	Thermally treated rice husk	Ni(II)	Adsorption	Farhan et al. (2017a, b)
10	Ceramic hollow fiber membrane	Heavy metals	Adsorption	Hubadillah et al. (2017)
11	Silica	Cr(VI)	Adsorption	Sivakumar (2015)

6.4.3 Organic pollutants

Currently, organic compounds (hydrocarbons, pesticides, antibiotics, residual polymers, etc.) are drastically polluting the water bodies. These pollutants are severely damaging the biosphere as well as interrupting atmospheric cycles (Ebrahiem et al. 2017). Thus, several materials have been designed for their removal, including RH derived adsorbents, such as activated carbon, silica, biochar, etc. AC has huge potential for removal of organic impurities due to large surface area, but the high production cost is a great hurdle in the way. Thus, RH has also been explored as a raw material for AC due to its low cost and perennial availability (Menya et al. 2018). The RH derived porous AC using NaOH was explored for removal of phenol (an organic pollutant) using the batch method. The AC has a 17.123 mg/g phenol removal capacity and follows pseudo-first order kinetics (Khan et al. 2017). The RH derived silica has been found in various shapes and sizes (Wang et al. 2011), which was further used for removal of different organic pollutants, such as hydrocarbons, pesticides, and antibiotics. The porous nature supports the adsorptive removal of organic compounds, which is effectively improved with reduction in the size of silica. The encapsulation of metal ions in silica develops catalytic behavior due to synergistic effects between silica and metal ions. Shukla et al. (2013) extracted silica with the size of 90 nm and high surface area and explored its suitability as a good adsorbent. Several other groups have improved the surface area and morphology of silica by adopting different chemical engineering. The obtained silica was used for purification of water from heavy metals, dyes, organic pollutants, and microbes (Roy et al. 2018; Zhang et al. 2017). Brief findings on the use of RH derived adsorbents for removal of organic pollutants are listed in Table 6.4.

Table 6.4 Removal of organic pollutants on RH derived adsorbents

S.N	Adsorbent	Pollutant	Capacity	Reference
1	Activated carbon	Phenol	17.123 mg g – 1	Wang, et al. (2011)
2	Biochars	Carbofuran	161 mg g^{-1}	Mayakaduwa et al. (2017)
3	Biochars	Polar herbicides	70.73 $cmol_c$/kg	Yavari et al. (2017)
4	Biochars	Imazapic and imazapyr	69.94%	Yavari et al. (2016)
5	Biochar	Phenol	67%	Komnitsas et al. (2016)
6	Ag loaded SiO2	Antibacterial	–	Cui et al. (2016)
7	Biochar	Tetracycline		Peiris et al. (2017)
8	Biochars	Carbofuran	25.2 mg g^{-1}	Vithanage et al. (2016)
9	Biochars	Levofloxacin	7.72 mg g^{-1}.	Yi et al. (2016)

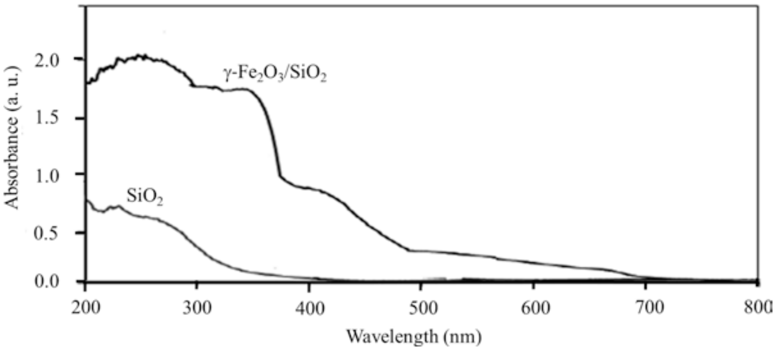

Fig. 6.5 Optical absorption spectra of SiO_2 and Fe_2O_3/SiO_2. (Fatimah et al. 2018a, b)

The synergism between RH and metal oxides adds an additional feature for water purification. For example, γ-Fe_2O_3 and SiO_2 aerogel have been fabricated using biogenic silica extracted from rice husk ash (RHA) with photocatalytic activity. The photocatalytic effect is due to band interactions between γ-Fe_2O_3 and SiO_2 that leads to the absorption at the visible region as shown in Fig. 6.5.

Thus, the obtained composite arogel was suitable for photo-Fenton-like degradation of rhodamine B(RhB). The photocatalytic activity in the photo-Fenton-like degradation of RhB reveals that γ-Fe_2O_3/SiO_2 aerogel demonstrates a similar degradation rate compared with γ-Fe_2O_3 nanoparticles along with the advantageous feature of stable reusability for three cycles (Fatimah et al. 2018a, b). Apart from AC and SiO_2, the BC is also prepared from RH and can be further modified by different methods, such as addition of metals. Addition of metals again generates a supportive strategy for purification of organic pollutants from water samples. The BC is a potential cost effective adsorbent for removal of oxyanions from wastewater. The BC shows porosity, large surface area, and chemical reactivates, which depend on biomass composition and extraction conditions for BC. The chemical modification of BC through metals has an advantageous role in antibiotic purification. Thus, several efforts have been made to prepare metal–biochar composites with high oxy-

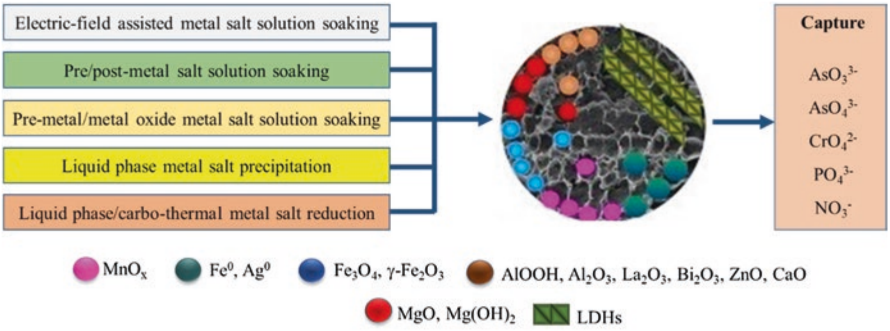

Fig. 6.6 Preparation of BC and metal composites (Li et al. 2018)

anion removal capacities. The impact of metal dosing and preparative conditions added several properties for purification of organic pollutants (Li et al. 2018). A simple strategy to prepare BC and metal composites is shown in Fig. 6.6.

Antibiotics are other very serious pollutants, which are increasing regularly due to biomedical wastes and antibiotic packaging systems. Their presence has been noticed in the water bodies and there is a growing concern about their physico-chemical impact as well as their biotic transformed products (Berkner et al. 2014). In this context, several methods such as advanced oxidation processes are developed for their control (Lofrano, et al. 2017). The RH developed adsorbents (BC) have been widely used for removal of the antibiotics tetracycline hydrochloride (TC), doxycycline hydrochloride (DC), and ciprofloxacin (CF). Zheng et al. explored the RH derived biochar for removal of three antibiotics. The capacity of antibiotic removal is directly related to the dosage amount and the surface area of biochar. Further, the pH and electrolyte behavior also affects the removal capacity. The adsorption isotherm follows the langmuir model mainly due to the chemical interaction between oxygen-containing functional groups (phenolic hydroxyl group, carboxyl, and alkoxy groups) of the biochar surface (Zeng et al. 2018).

6.4.4 *Microbes*

Microbes are another group of water polluting agents, whichdevelop in due course of time. They are responsible for several diseases, such as cholera, dysentery, typhoid, etc. The adsorbents prepared from RH are found to be very important for control of microbial pollution. A microbial biotreatment method for actual textile wastewater uses a continuous sequential biofilter using rice husk for removal of a developed microbial community. In this regard, RH has been found effective against a multidrug-resistant strain of *Salmonella* Typhimurium. The antibacterial activity of RH results from a leakage of intracellular macromolecules following rupture of bacterial cells (Kim et al. 2018). The RH derived silica also has the ability to remove several strains of microorganisms from the water like *Escherichia coli*, Bacillus subtilis, *Candida albicans*, *Pseudomonas aeruginosa*, *Staphylococcus aureus,* and freshwater heterotrophic bacterial association. The microbe removal ability is related to physical and chemical parameters, such as composition, specific surface value, pore size, zeta potential value, and surface hydrophobicity. Better microbe removal efficiency of SiO_2 has been reported for different strains of microorganisms than other available commercial sorbents. The extent of bacterial cells adsorption on biogenic silica is higher at lower pH (Zemnukhova et al. 2015). Chemically modified silica has also been explored for removal of different microbes. Hey et al. impregnated silver ions into a rice husk derive silica matrix. The size of impregnated AgNPs is ~20 nm, which is anchored tightly onto RHA. The emplacement of silver nanoparticles into silica increases the antibacterial activity. This type of bactericidal "lifetime" exhibits long life and lower health risk as a result of the release of Ag(I) to consumers (Menya et al. 2018). Similarly, addition of TiO_2 in the silica matrix enhances the bactericidal capability capacity for purification of water. The biotemplated hierarchical porous material derived from rice husk offers an example for removal of bacteria. It adds an advancement in new functional materials for enhanced bacterial elimination (He et al. 2013). The combination of the high adsorption capacity of ACs with the magnetic properties of nano-sized iron oxide is also explored as a promising composite material. This composite material has been advocated as a substitute adsorbent colonized in small bioreactors (Yang et al. 2014).

6.4.5 Miscellaneous

The other important pollutants that are removed by RH-based adsorbents are organic and inorganic gases, such as indoor toxic pollutant gases trimethylamine (TMA) and H_2S. These gases are fatal to humans, even from exposure to very small concentration. The RH-derived porous carbon was explored to develop a carbon-based filter for sustainable use of a biomass waste. The thermal treatment conditions, such as carbonization temperature, affect the surface area of derived activated rice husk carbon (ARH) as well as adsorption of pollutant gas. The impregnation of copper in the activated (Cu/ARH) carbon makes it more suitable for adsorption and removal of toxic gases present in an enclosed chamber. The Cu/ARH-based filter was able to remove 400 ppm of TMA in 30 min and H_2S in 15 min. The adsorption of these gases follows the pseudo-second order kinetic model as well as intra-particle diffusion and Yoon-Nelson kinetic models with the possibility for successfully regeneration. The H_2S adsorbed Cu/ARH filter was successfully regenerated, whereas a TMA adsorbed Cu/ARH filter was not successfully regenerated (Lompe et al. 2016). Further, the adsorption behavior of RH carbon-based materials for removal of natural organic matter (NOM) from water influences the design of filters (Fig. 6.7). However, the major limitation is the high cost of production and regeneration; thus, it is pertinent to design low cost methods for production of carbon-based materials from RH (Nam et al. 2018).

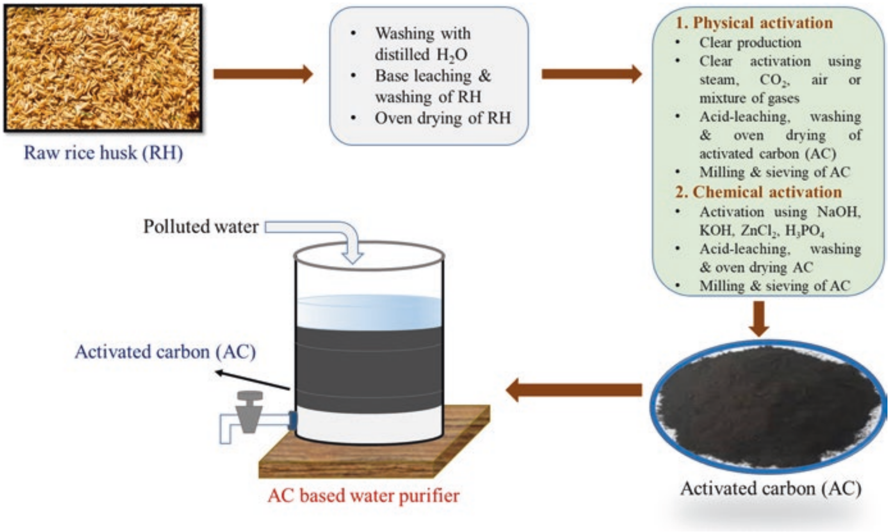

Fig. 6.7 Schematic diagram for designing an AC based filter. (Redrawn from Menya et al. 2018)

The chemical functionalization of RH is another way to improve the adsorption efficiency of activated carbon (AC) due to optimization in solvation and adsorption energy. The functionalized AC at different bonds (C=C, Si–O–Si, O–H, and C–O(H)) has been used for adsorption of 16 VOCs lying in the range of 4.0–6.1 (g g^{-1})/(g mL^{-1}) under medium RH (around 55%), but decreased under high RH (90%). It reveals that the AC is a promising adsorbent for removal of several organic compounds (Li et al. 2016). Similarly, the capacity of BC derived from RH has also been explored for removal of gaseous ozone, adsorbed nitrate, and aqueous bisphenol A (BPA). The removal depends on the heterogeneous chemistry of ozone and nitrate on the surface of biochar. The BC indicates excellent ability for removal of ozone by 55 ppb without formation of any volatile by-products during the reaction. The adsorption of nitrate produces reduced nitrogen oxides (NO and NO_2). However, photoreduction of nitrate induces the formation of reduced carbon on the surface of BC and it leads to the formation of nitrite (Zhou et al. 2018).

6.5 Conclusion

Rice husks, which are widely available perennially, have been explored for development of different water purifying materials, such as silica, biochar, activated carbon, etc. These materials are found highly useful for purification of water from dyes, heavy metals, microbes, and other organic pollutants. The adsorbents were further modified by addition of chemicals such as metals for better removal of water pollutants. The published data indicates that rice husks have great potential for development of cost effective adsorbents for efficient removal of water pollutants due to their low cost and perennial production in most parts of the world.

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Chapter 7
Treatment of Dye Containing Wastewater Using Agricultural Biomass Derived Magnetic Adsorbents

A. Saravanan, P. Senthil Kumar, and P. R. Yaashikaa

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Abstract As of late, different mechanical exercises have genuinely contaminated the earth. Because of the low working expenses and high adaptability, adsorption is considered as a standout amongst the best advances for poison administration. Agricultural waste has free and permeable structures and contains utilitarian gatherings, for example, the carboxyl gathering and hydroxyl gathering, so it can be considered as an organic adsorption material. Agrarian waste has the benefits of an extensive variety of sources, it requires minimal effort, and it is sustainable. It has a decent prospect for the far-reaching usage of assets when utilized for natural con-

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A. Saravanan
Department of Biotechnology, Rajalakshmi Engineering College, Chennai, India

P. Senthil Kumar (✉) · P. R. Yaashikaa
Department of Chemical Engineering, SSN College of Engineering, Chennai, India

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tamination control. Attractive partition of lethal toxins is turning into a potential technique in wastewater treatment and is found to have prevalent criticalness in the evacuation of dyes even more so than regular techniques for medicines. Various characteristics and engineered adsorbents were utilized. This chapter talks about the amalgamation of magnetic adsorbents from rural waste and their applications in overwhelming dye expulsion. The general strategies for preparing attractive adsorbents and the components of overwhelming dye sorption are additionally investigated in detail. The resultant agricultural biomass inferred attractive adsorbents displayed a permeable structure with a higher particular surface area and more oxygen-containing practical gatherings than its carbonaceous antecedent. Along these lines, this chapter proposes magnetic-based materials as potential contenders for wastewater treatment.

Keywords Wastewater treatment · Dye removal · Adsorption · Magnetic biosorbents · Agro biomass

7.1 Introduction

With the rapid advancement of industry and the over-abuse of regular assets, natural contamination has caused genuine damage to human wellbeing; therefore, it is pressing to tackle biological issues (Jawad et al. 2015). Water bolsters life for man, creatures, and plants. However, the area of clean water accessible to humankind is contracting. One of the essential drivers of this is the contamination of numerous freshwater assets (Sharma et al. 2018). The dirty lakes and waterways have turned out to be contaminated with a variety of waste, including untreated or in part treated metropolitan sewage, toxic mechanical effluents, destructive synthetics, and ground waters from agrarian exercises. Dirtied water decides the water accessibility, as well as puts millions in danger of water-related ailments (Sivashankar et al. 2014).

Dyes are essentially substance aggregates that can associate themselves to surfaces or textures to give shading. The greater part of dyes comprises unpredictable natural atoms and is required to be impervious to numerous things, such as the activity of cleansers. Release of these colors into effluents affects the general population who may utilize these effluents for living purposes, for example, washing, showering, and drinking. In this manner, it is extremely essential to check the water quality, particularly when even only 1.0 mg/L of dye concentration in drinking water could bestow a huge shading, making it unfit for human utilization (Malik et al. 2007; Adegoke and Bello 2015).

Synthetic dyes are generally utilized as a part of numerous fields of innovation, e.g., in different sorts of textile, paper, tanning, pharmaceutical, plastics, beauty care products, elastic, food processing, printing, and dye fabricating enterprises (Wrobel et al. 2001; Bensalah et al. 2009; Yagub et al. 2014; Nidheesh et al. 2018).

As of now, synthetic dyes wind up as one of the significant contaminates in mechanical effluents. The vast majority of colors in the effluents contain nondegradable fragrant structures, and are thought to be lethal and indeed even carcinogenic, which brings about negative impacts on human wellbeing and environmental security.

Consequently, the treatment and transfer of color containing wastewater is direly required and has stimulated overall concern (Thakur et al. 2017). The arrival of fundamental measures of manufactured dyes to the earth has posed difficulties to natural researchers. Among all the distinctive methodologies for expelling dyes from water, including substance (oxidation, coagulation, and so on), physical (adsorption, filtration, particle trade, illumination, and so on), and organic techniques (microbial staining), adsorption stands out for its effortlessness and wide assortment of existing adsorbent frameworks (Gupta 2009; Shuang et al. 2012), and it is amongst the best procedures of innovative wastewater treatment, which ventures to lessen dangerous inorganic/natural contaminations shown in the flow (Sharma et al. 2017; Saravanan et al. 2017, 2018).

7.2 Classification of Dyes

Dye molecules contain two key segments: the chromophores, in charge of creating the shading, and the auxochromes, which can supplement the chromophore as well as render the particle dissolvable in water and give improved affinity around the strands. Dyes display an impressive auxiliary assorted variety and are ordered in a few different ways. It ought to be noticed that each class of dye has an exceptionally one of a kind science, structure, and specific method for holding (Gregory 1990). While a few dyes can respond synthetically with the substrates shaping solid securities all the while, others can be held by physical powers. A portion of the conspicuous methods for characterization is given hereunder.

- Classification in light of the wellspring of materials.
- Chemical arrangement of the dyes based on the idea of their separate chromophores.
- Dyes as indicated by the atomic structure.
- Industrial classification of the dyes.

7.2.1 Grouping in View of the Wellspring of Materials

An extremely basic order of the dyestuff depends on the source from which it is made. In like manner the grouping could be:

(a) Natural dyes.
(b) Synthetic dyes.

7.2.1.1 Natural Dyes

Man has utilized shading materials for a large number of years. Cowhide, fabric, nourishment, ceramics, and lodging have all been adjusted along these lines. The two old courses were to cover with a shade (painting) or to shade the entire mass (coloring). Shades for painting were normally produced using ground up hued rocks and minerals, and the dyes were acquired from creatures and plants. Today, a significant number of the conventional dye sources are occasionally, if at any time, utilized (onionskins, for example). In any case, a portion of our most normal dyes is yet gotten from characteristic sources. These are named natural dyes.

These dyes are in this manner particularly distinguished as dyes of the expressed shading, which may at present be obtained from creatures or plants. Note this is a grouping in light of the dye's source and shading. It contains no substance data; neither does it infer that dyes with comparative names yet interesting numbers are in any capacity related. It gives no data about the system by which recoloring happens.

Natural dyes are regularly contrarily charged. Emphatically charged natural dyes do exist; however, they are not normal. As it were, the shaded piece of the atom is typically the anion. In spite of the fact that the sub-atomic charge frequently appears on a particular iota in auxiliary formulae, the entire particle is charged. Many, however, in no way, shape or form every single, characteristic dye requires the utilization of an astringent.

7.2.1.2 Synthetic Dyes

Synthetic dyes are utilized in everything from garments to paper, from sustenance to wood. This is because they are less expensive to create, brighter, shade more quickly, and are simple to apply to texture. Examples of this class of dyes are direct, acid, basic, reactive, mordant, metal complex, vat, sulfur, disperse dye, etc.

Acid Dyes

Corrosive (anionic) dyes are water-dissolvable dyes connected to fleece, silk, nylon, adjusted rayon, certain altered acrylic, and polyester filaments. Filaments that will be harmed by acids, for example, cellulosics, cannot be colored with this group of dyes. The dyes in this class differ in their makeup yet all utilize a corrosive shower. These colors create brilliant hues and have a total shading range; however, colorfastness fluctuates.

Azoic Dyes

Azoic (naphthol) dyes are created inside the fiber of cellulose filaments. The fiber is impregnated with one part of the dye, trailed by treatment with another segment, along these lines forming the dye. At the point when the two segments are joined under appropriate conditions (a low temperature water shower is utilized) an expansive, insoluble, shaded atom forms inside the fiber.

Basic Dyes

Basic (cationic) dyes are brilliant but have poor colorfastness, and they have constrained use on cellulosic and protein filaments. Fleece and silk can be colored by basic dye in a color shower containing a corrosive. Cotton filaments can be colored by essential dyes; however, just within the presence of an astringent, largely a metallic salt. The shaded part of the color atom conveys a positive charge. Basic dyes are moderately colorcast on acrylic strands. Nylon and polyester filaments that have been adjusted to acknowledge fundamental colors will show amazing colorfastness.

Direct Dyes

Direct (substantive) dyes are solvent and have an affinity for cellulose strands. An electrolyte, salt, is added to the color shower to control the ingestion rate of the color by the fiber. Direct dyes are best utilized when wet cleaning is limited. Grown direct dyes are those that are created on the texture in the wake of coloring. They deliver an insoluble dye that structures a synthetic bond with the fiber atoms. Grown direct dyes have better wash quickness but poorer light speed than direct dyes. Both are utilized to bring down the cost of textures.

Disperse Dyes

Disperse dyes were first created to dye acetic acid derivation strands. Hydrophobic filaments have little affinity for water-dissolvable dyes. A technique to dye hydrophobic filaments by scattering hued natural substances in water with a surfactant was generated. The finely shaded particles are connected in watery scattering and the shading breaks down in the hydrophobic fiber. Disperse dyes are the best technique for dyeing acetic acid derivations and polyester. Acrylic, aramid, modacrylic, nylon, olefin, and polyester are colored by scattered colors; colorfastness is amazing.

Pigment Dyes

Pigment dyes are not dyes but rather insoluble shading particles. Dyes are added to the turning arrangement (the fluid fiber before expulsion) of manufactured strands and turn into an essential piece of the fiber. Colorfastness is brilliant. Shades are likewise imprinted on texture utilizing pitch covers. The cement appends the shading to the texture. Colorfastness is reliant on the fastener or glue utilized as opposed to the shade. Shade printing is a conservative and basic method for adding shading to textures.

Reactive Dyes

Reactive (fiber-receptive) dyes join with fiber atoms by either expansion or substitution. The shading cannot be expelled if legitimately connected. Dyes are bright with great colorfastness; however, they are defenseless to harm by chlorine blanches. Reactive dyes shading includes cellulosics (cotton, flax, and gooey rayon), silk, fleece, and nylon. Reactive dyes are utilized in conjunction with scatter colors to color polyester and cellulosic fiber mixes.

Sulfur Dyes

Sulfur dyes are insoluble yet turned out to be solvent in sodium polysulfide. They have superb colorfastness in water. Another preferred standpoint is their minimal effort and simplicity of use. Dim shades—dark, brown, naval force blue—are normal for sulfur colors. More up-to-date sulfur dyes are accessible in brighter hues.

Vat Dyes

Vat dyes are insoluble in water yet end up dissolvable when diminished within the presence of an antacid. Oxidizing the colored texture delivers a water insoluble dye. The term vat dyes is taken from the extensive vessels used to apply the dye. The primary engineered indigo dye, introduced to the business in 1896, has a place in this class. Vat dyes have an inadequate shading range yet are great for brilliant colorfastness. They are principally used to dye cotton work garments, sportswear, prints, drapery textures, and cotton–polyester mixes.

7.3 Toxic Effect of Dyes

Dyes can influence aquatic plants since they lessen daylight transmission through water. Likewise dyes may pose a danger to amphibian life and might be mutagenic, carcinogenic, and may cause serious harm to people, for example, failure of the kidneys, regenerative framework, liver, mind, and focal sensory system. The dye materials have destructive impacts, as well as being tastefully unsavory in water. The dyes utilized as a part of the material industries include a few structure assortments, for example, acidic, reactive, essential, scatter, azo, diazo, anthraquinone-based, and metal complex dyes (Jothirani et al. 2016; Kausar et al. 2018).

The dyeing procedure includes a considerable measure of water, and not all spots have successful methods for cleaning the water before it returns into the earth. Wastewater from material dyeing is a tremendous toxin around the globe. A few dyes never degrade in water, while others that do deliver unsafe substances as they deteriorate. Added substances utilized amid the dyeing procedure include unsafe substances, for example, soluble bases and corrosives (Gupta and Suhas 2009; Dawood and Sen 2013; Raman and Kanmani 2016; Suganya et al. 2017). Wastewater from material dyeing likewise influences vegetation in the water, in light of the fact that numerous dyes have substances that reduce photosynthesis, the procedure by which plants get nutrients.

7.3.1 Environmental Impacts

Dye is typically the main contaminant to be perceived in wastewater on the grounds that a small measure of engineered colors in water (<1 ppm) are very unmistakable, influencing the taste legitimacy, straightforwardness, and gas dissolvability of water bodies. They adsorb and mirror the daylight entering water, along these lines meddling with sea-going species development and impeding photosynthesis. In addition, they can have intense and/or on the other hand endless impacts on living beings depending upon their fixation and length of presentation (Rodriguez-Couto et al. 2009; Katheresan et al. 2018). Expulsion of dye from color containing wastewater is the first and major concern; however, the purpose of degrading colors is not just to expel shading but to eliminate, or considerably diminish, the poisonous quality (Gupta 2009; Kant 2012; Pereira and Alves 2012; Patra et al. 2018).

The most well known risk of receptive dyes is respiratory issues due to the inhalation of color particles. At times, they can influence an individual's invulnerable framework, and in outrageous cases, this can mean that when the individual next breathes in the dye their body can respond drastically. This is called respiratory refinement, and side effects include tingling, watery eyes, wheezing, and side effects of asthma, for example, hacking and wheezing (Hassaan and Nemr 2017).

Maybe the most dominating medical issues identified with dyeing and completing procedures emerge from introduction to synthetic concoctions going about as aggravations. These may cause skin irritation, bothersome or blocked noses, wheezing, and sore eyes. They include formaldehyde-based saps, smelling salts, acidic corrosives, a few anti-wrinkle synthetics, some optical whiteners, pop fiery debris, scathing pop and fade. Certain responsive, vat, and scatter dyes are likewise perceived as skin irritants (Yao et al. 2014; Nidheesh et al. 2018). The azo dyes are observed to be mind boggling in nature and have been found to indicate carcinogenic confirmations on reductive cleavage. These dyes are equipped for adjusting the physical and compound properties of soil, falling apart in water bodies and hurting the widely varied vegetation on the earth. It was seen that poisonous dyes cause the demise of dirt microorganisms, which thusly influences the horticultural profitability (Hassaan et al. 2015, 2017).

7.3.1.1 Air Pollution

Most procedures performed in material plants create environmental outflows. Vaporous outflows have been recognized as the second most noteworthy contamination issue (after flow quality) for the material businesses. Theory concerning the sums and sorts of air toxins radiated from material tasks has been boundless; be that as it may, by and large, air emanation information for material assembling activities are not promptly accessible. Air contamination is the most troublesome kind of contamination to test and measure in a review.

7.3.1.2 Water Pollution

The wastewater from material plants is delegated the dirtiest of all the mechanical parts, considering the volume produced and the flow structure. What's more, the expanded interest for material items and the corresponding increase in their creation and the utilization of manufactured colors have together added to color wastewater becoming one of the significant wellsprings of serious contamination issues today (Kumar et al. 2014a, b; Natarajan et al. 2018). Dyes can stay in the earth for an extended timeframe due to high warmth and strength to oppose bio degradation.

7.3.1.3 Hurtful Impact of Dyes

Dyes ingest and reflect daylight in water. This reduces photosynthetic movement of green growth and genuinely affects the evolved way of life.

- Many dyes and their breakdown items are carcinogenic, mutagenic, as well as poisonous to life.
- Various diseases, including skin, kidney, urinary bladder, and liver, of dye laborers have been accounted for.
- Textile dyes can cause hypersensitivities, for example, contact dermatitis and respiratory illnesses, unfavorably susceptible response in eyes, skin irritation, and bothersome to mucous film and the upper respiratory tract.
- Certain responsive dyes cause respiratory refinement of laborers who are occupationally exposed to them.
- The nearness of little measures of dyes in the water genuinely influences the quality and straightforwardness of water bodies, for example, lakes, streams, and others, and harms the oceanic condition.
- The profoundly harmful and mutagenic dyes diminish light infiltration and photosynthetic action, causing oxygen insufficiency and restricting downstream advantageous uses, for example, entertainment, drinking water, and water systems.
- Azo dyes have lethal impacts, particularly carcinogenic and mutagenic. They enter the body by ingestion and are processed by intestinal microorganisms causing DNA harm.

7.4 Conventional Treatment Methodologies

There are various techniques to treat dye-bearing effluents. Despite the numerous procedures to expel dye contaminants from wastewaters, for example, coagulation, photo-degradation, chemical oxidation, membrane separation process, electrochemical and aerobic and anaerobic microbial debasement, every one of these strategies have natural impediments (Pathania et al. 2016; Kumar 2010; Kumar et al. 2011; Premkumar et al. 2013). These days, the worry is fundamentally centered on creating economical and powerful techniques to treat wastewater released from the enterprises to ensure amphibian life in water bodies. Along these lines, the techniques could be physio-compound, biochemical or a mix of both, which can give viable advancements in expelling contaminants from wastewater originating from businesses. Existing strategies for dye evacuation can be isolated into three classes, specifically the biological, chemical, and physical treatments (Katheresan et al. 2018; Tang et al. 2018).

7.4.1 Biological Dye Expulsion Strategies

The regular biological strategy is the commonly and widely used dye evacuation technique to treat dye wastewater. For the most part known as the regular strategy, a mix of oxygen consuming and anaerobic processes are completed before color effluents are discharged to the earth. The biological degradation (i.e., bioremediation) is financially achievable, naturally inviting, and creates less volume of slime when contrasted with other procedures (Martorell et al. 2017). It degrades synthetic dyes into relatively less poisonous inorganic compounds because of the breakdown of bonds (i.e., chromophoric gathering) and helps in expulsion of shading (Bhatia et al. 2017).

7.5 Adsorption

Adsorption is a surface wonder, which emerges because of collaborations between the singular particles—particles or atoms of an adsorbate and those present in the adsorbent surface. Adsorption is a procedure that happens when a gas or liquid solute amasses on the surface of a solid or a liquid (adsorbent), framing a sub-atomic or nuclear film (the adsorbate). The procedure includes a variety of wonders that can change the dissemination of the solute among the constituent stages and in the interfaces (Ponnusamy and Subramaniam 2013; Kumar et al. 2014a, b; Low and Tan 2018; Mousavi et al. 2018; Othman et al. 2018; Sham and Notley 2018). Connection of adsorbate atoms at practical gatherings on an adsorbent surface can likewise result from particular collaborations, which do not result in adsorbate change. The cooperation displays a scope of restricting energies from values related with physical adsorption to the higher energies associated with chemisorption. The net scattering, electrostatic, chemisorptive, and functional group communications extensively characterize the capacity of an adsorbent for a particular adsorption.

The term adsorption alludes to the gathering of a substance at the interface between two stages. The substance that gathers at the interface is called adsorbate and the surface on which adsorption happens is adsorbent. Adsorption can be arranged into two sorts: chemical sorption and physical sorption.

7.5.1 Chemical Adsorption

Chemisorption is outlined by the development of a relationship between particles of adsorbate and the adsorbent surface, which is for the most part due to the trading of electrons, and in this manner, concoction sorption is mostly irreversible. Chemical adsorption includes solid adsorbate–adsorbent communications bringing about an adjustment in the substance type of the adsorbate. Here, the gas particles or molecules are held to the solid surface by concoction bonds (Liu et al. 2017). The subsequent chemisorptive bond is for the most part more grounded than that obtained from the physical van der Waals powers and is fundamentally the same in quality as a covalent bond. It is exceedingly particular and happens just if there is some probability of synthetic holding amongst adsorbent and adsorbate. The bonds that form between solute particles and particular surface synthetic gatherings have every one of the properties of genuine synthetic bonds and are described by moderately substantial warming of adsorption.

7.5.2 Physical Adsorption

Physisorption is portrayed by feeble van der Waals intraparticle bonds amongst adsorbate and adsorbent and in this manner reversible as a rule. Adsorption on the majority of the adsorbent including farming results is controlled by physical powers with some special case of chemisorption. This procedure gives an appealing option for the treatment of dirtied waters, particularly in the event that the sorbent is modest and does not require an extra pre-treatment before its application (Du et al. 2014; Mu and Wang 2016). With respect to the ecological remediation reason, adsorption methods are generally used to expel certain classes of concoction contaminants from waters, particularly those that are unaffected by regular organic wastewater medicines (Dabrowski 2001; Yagub et al. 2014).

In adsorption, there are two components present in the adsorption process. (i) Adsorbate and (ii) Adsorbent.

The adsorbent must have great mechanical properties, for example, quality and protection from steady loss, and it must have great active properties, that is, it must be able to exchange adsorbing particles quickly to the adsorption destinations. An adsorbent material must have a high inward volume, which is open to the segments being expelled from the dissolvable. Surface area and the appropriation of area regarding pore measure are two critical factors in deciding degree of adsorption. The idea of the intraparticle surface zone especially affects the kind of adsorption process.

The degree of adsorption identifies with specific properties of the adsorbate with respect to the arrangement stage, in particular surface pressure and solvency. Adsorbents are for the most part obtained from sources, for example, zeolites, charcoal, muds, metals, and other waste assets. Adsorbents arranged from water resources utilized coconut shell, rice husk, oil squanders, tannin-rich materials, sawdust, manure wastes, fly powder, impact heater slag, chitosan and fish handling squanders, ocean growth and green growth, peat greenery, scrap tires, organic product wastes, and so on.

7.6 Agricultural Biomass

Biosorption of dye from watery arrangements is a generally new process that has demonstrated extremely encouraging results in the expulsion of contaminants from fluid effluents. Adsorbent materials obtained from minimal effort agricultural waste biomass can be utilized for the compelling expulsion and recuperation of toxic dye from wastewater streams.

The term biomass alludes to wood, short-pivot woody yields, agrarian waste, short rotation herbaceous species, wood waste, bagasse, mechanical buildups, waste paper, metropolitan solid waste, sawdust, biosolids, grass, nourishment preparing waste, amphibian plants, green growth creature waste, and a large group of different materials.

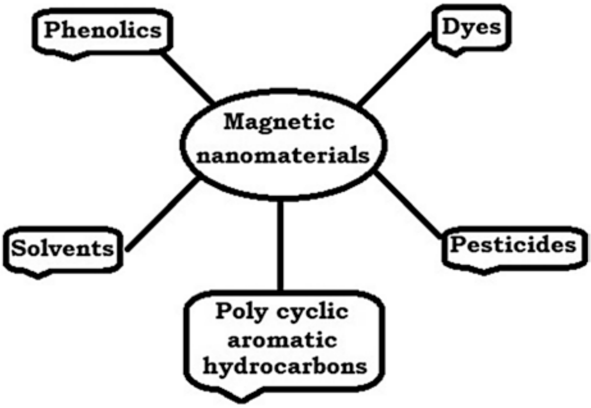
The fundamental segments of the rural waste materials include hemicelluloses, lignin, lipids, proteins, basic sugars, water, hydrocarbons, and starch, containing an assortment of useful gatherings with a potential sorption limit with respect to different contaminations (Loannidou et al. 2010). Rural waste items are utilized in the regular and adjusted form. In the characteristic form, the item is washed, ground, and sieved until it comes to the coveted molecule size and consequently is utilized in adsorption tests, while in the changed form, the item is pre-treated by methods for surely understood adjustment strategies. The objective of these pre-treatments is to upgrade and fortify the practical gathering potential further; therefore, increasing the quantity of dynamic destinations. Agrarian waste items have been widely examined in connection to the adsorption process. Beneath, the most noteworthy encounters are depicted, beginning with horticulture and family unit waste sorbents for the expulsion of colors from single compound fluid arrangements.

Cellulose is a momentous unadulterated natural polymer, comprising exclusively units of anhydroglucose held together in a goliath straight chain particle. By shaping intramolecular and intermolecular hydrogen bonds between OH bunches inside a similar cellulose chain and the encompassing cellulose chains, the chains have a tendency to be masterminded parallel and form a crystalline super molecular structure. At that point, packs of straight cellulose chains (in the longitudinal course) form a micro fibril, which is arranged in the cell divider structure. Cellulose is insoluble in many solvents and has a low availability to corrosive and enzymatic hydrolysis. Not at all like cellulose, hemicellulose comprises various monosaccharide units. What's more, the polymer chains of hemicelluloses have short branches and are formless. In light of the indistinct morphology, hemicelluloses are incompletely soluble or then again swellable in water. Hemicelluloses are identified with plant gums in organization; furthermore, they happen in substantially shorter particle chains than cellulose. Hemicelluloses are principally obtained from chains of pentose sugars, and also from the bond material holding together the cellulose micells and fiber. Lignins are polymers of fragrant mixes. Their capacities are to give basic quality, fix the water leading framework that connects roots with leaves, and secure plants against degradation. Lignin is a macromolecule, which comprises alkylphenols and has an unpredictable three-dimensional structure. Lignin is covalently connected with xylans in hardwoods and with galacto glucomannans in softwoods.

7.7 Magnetic Adsorbent from Agro Biomass

In the most recent decade, thorough examinations and advancements were seen in the field of nano-sized attractive particles. These materials frequently have special electrical, concoction, basic, and attractive properties taking into account use in the field of novel applications, including data capacity, sedate conveyance, biosensors, substance and biochemical partition, and natural remediation. Figure 7.1 shows the magnetic materials for organic degradation.

Fig. 7.1 Representation of different natural materials degraded by magnetic nanoparticles



Magnetic adsorbents have been produced as an option for innovation of wastewater treatment, which refers to natural substances as attractive transporters that can be effectively utilized in evacuating contaminants. Attractive transporters have restricting locales for natural particles and display attractive properties. Among other marvels, the attraction to the atoms can happen by adsorption. The blend of these two properties, adsorption and attraction, into one composite enables acquiring an attractive adsorbent conceivably relevant in wastewater treatment (Yu et al. 2016; Noor et al. 2017). This composite can be utilized to adsorb contaminants and hence can be evacuated from the medium by an attractive detachment technique utilizing an outer attractive field and without the utilization of filtration or centrifugation. The adsorbent substrates of the attractive adsorbents can be characteristic or engineered materials, which have indicated proficiency in evacuating dyes. Figure 7.2 shows the overview of adsorption of dye using magnetic adsorbents.

The utilization of magnetism for water filtration is a deep-rooted idea. From that point, forward attraction has been utilized in different water treatment techniques, for example, harsh scaling procedure in boilers, pipelines in production lines, coagulation, and natural procedures. The utilization of attraction in an adsorption procedure is a moderately more up-to-date idea; one that is gathering expanding consideration from the specialists systematically. Attractive adsorbents are another class of adsorbents where a base adsorbent is installed with attractive particles, which are dye oxides.

Unadulterated inorganic magnetic particles are helpless to gathering of cross sections; totals that may change their attractive trademark. The impediments of utilizing magnetic particles in the recuperation of dyes include low selectivity toward target dyes in complex grids and shaky particles in solid acidic arrangements. A surface adjustment of an appropriate practical gathering of the attractive center has been considered to address these confinements. The attractive center is covered with a shell that can either be inorganic (e.g., silica or alumina) or natural atoms (e.g., changed with polymer or surfactant and so on), keeping in mind the end goal to enhance its compound soundness, protection from oxidation, and increase the selectivity toward target dyes. Moreover, surface functionalization of attractive particles can be proficient by fusing natural or inorganic utilitarian gatherings onto an inorganic shell enhancing the sorption ability.

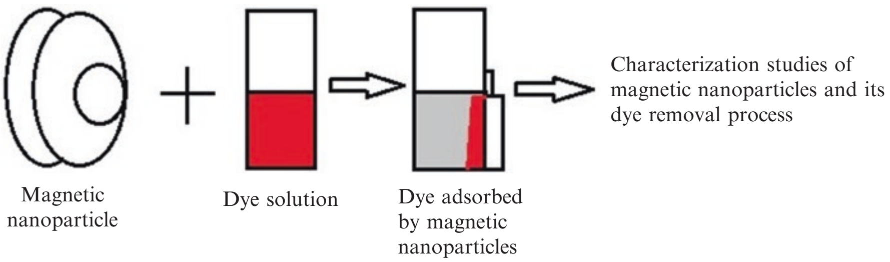


Fig. 7.2 Adsorption of dye using magnetic nanoparticles

There are two basic ways to deal with delivery of an attractive adsorbent, to be specific, concoction co-precipitation and pyrolysis at divergent febricities. A blend of the two strategies to deliver attractive biochar or attractive actuated carbon is additionally supported. The blend of pyrolysis and co-precipitation begins with the precipitation of biomass, followed by synthetic compounds to make strides in the adsorption capacity of the biomass. At that point, the biomass is carbonized at various temperatures (typically below 800 °C), without oxygen to build its porosity and surface area. Different strategies to integrate attractive adsorbents include co-precipitation, warm deterioration, aqueous, polyol process, sol–gel, and substance lessening.

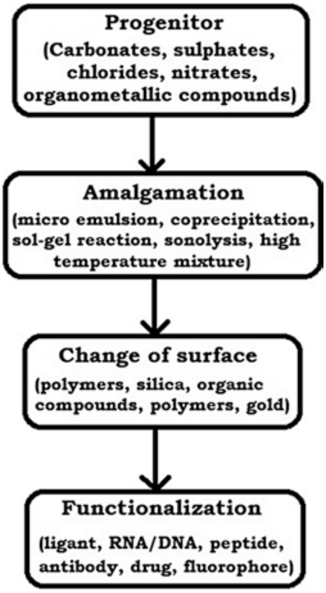
Magnetic nanoparticles (MNPs) are a class of nanoparticles that can be controlled utilizing a magnetic field. MNPs have the upsides of vast surface area, high number of surface dynamic locales, and high attractive properties, which cause high adsorption productivity, high evacuation rate of contaminants, and simple and fast partition of adsorbent from arrangement through attractive field. Figure 7.3 shows the outline of the magnetic particles process.

After attractive detachment, the desorbent specialists can effortlessly expel the contaminants from nanoparticles, and the recouped MNPs can be reused.

The surface change procedure of magnetic particles for the most part contained three stages.

1. Arrangement of the attractive sorbent (magnetite or maghemite);
2. Layering of the attractive center with a shell-like system and;
3. Functionalization of the resultant center shell structure.

Fig. 7.3 The outline of the magnetic particles process



The adsorption utilizing magnetic adsorbents includes the expansion of magnetic sorbent particles to the solution. The objective compound is adsorbed onto the magnetic material and the magnetic molecule (containing the analyte) is then isolated from the example arrangement by the utilization of an outer attractive field. Finally, the analyte is recouped from the adsorbent by elution with the fitting dissolvable and is hence examined. Figure 7.4 represents the entire procedure of adsorption using magnetic adsorbents.

This approach has a few points of interest over customary solid phase extraction:

1. It maintains a strategic distance from tedious and repetitive on-segment solid phase extraction methodology,
2. It gives a quick and straightforward analyte detachment that evades the requirement for centrifugation or filtration steps,
3. The attractive sorbents orchestrated to date have high selectivity, notwithstanding when complex grids from natural or organic fields were used,
4. Since the larger part of test polluting influences are diamagnetic, they do not meddle with attractive particles amid the attractive partition step, and
5. Mechanization of the entire procedure is conceivable with flow infusion investigation and other related strategies, which prompts fast, particular, delicate, and repeatable techniques for routine judgments. Figure 7.5 represents the schematic presentation of magnetic solid phase extraction.

These favorable circumstances could be accomplished as consequences of properties of attractive nanoparticles including:

1. High extraction effectiveness due to the high surface-to-volume proportion of the extraction stage;
2. Quick partition after extraction contrasted with regular solid phase extraction techniques;
3. Comfort of planning and surface adjustment of the extraction stage (e.g., exposed Fe_3O_4 can be essentially and quickly arranged by co-precipitation or aqueous amalgamation, and can be advantageously changed with practical gatherings as a result of the bounteous hydroxyls on the surface of Fe_3O_4 nanoparticles);
4. High selectivity of the objective analytes and reasonableness for the confused grids (appropriate covering not only balances out the nanoparticles and main-

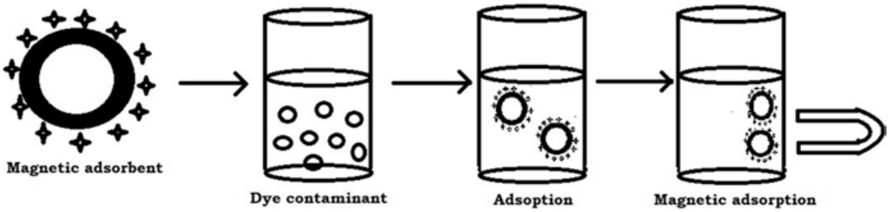


Fig. 7.4 Representation of the entire procedure of adsorption using magnetic adsorbents

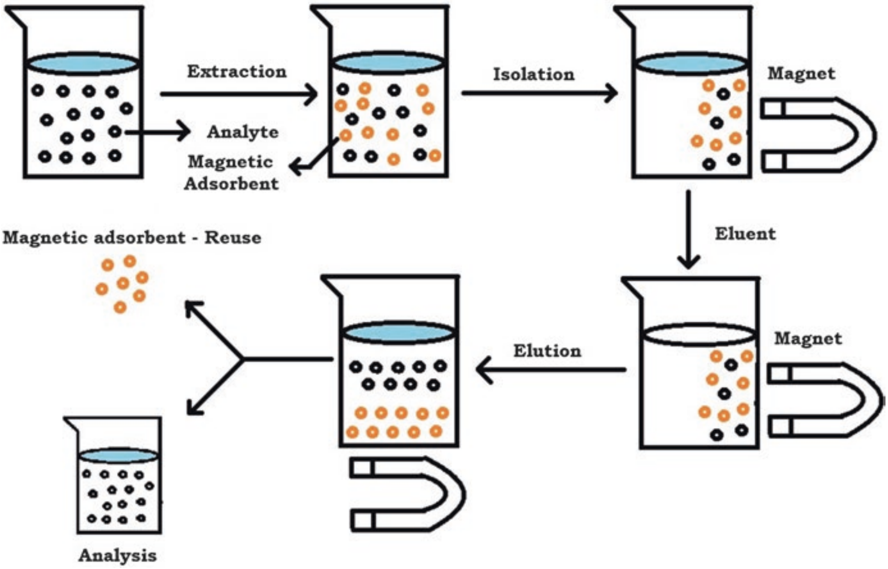


Fig. 7.5 Schematic presentation of magnetic solid phase extraction

tains their oxidation but also gives particular functionalities that can be specific for analytes);

5. Great reusability (attractive particles can be reused after fitting washing);
6. Incredible dispersibility in watery arrangement and simple to work with.

7.7.1 Pyrolysis

Regular pyrolysis is likewise usually used to deliver attractive biochars. This technique exchanges warmth between objects through conduction, radiation, and convection. In this manner, the surface of the material is first warmed, followed by the warmth moving internal. This implies there is a temperature angle from the surface to within the material. Rather than utilizing a solitary course amalgamation, customary pyrolysis comprises two procedures, in particular, carbonization and enactment. Carbonization includes the development of a non-permeable scorch by means of pyrolysis of the antecedent at a temperature that reaches somewhere in the range of 600–900 °C in dormant air. The second stage (enactment) includes reaching the burn with an oxidizing gas, for example, CO_2 or steam at 600–1200 °C, which would expel the more scattered carbon, and the arrangement of an all-around created micropore structure.

7.7.2 Co-precipitation

The most well-known and proficient strategy of preparing an attractive adsorbent is the co-precipitation technique. The upsides of this strategy include basic arrangement, more straightforward response conditions, and higher item virtue. In any case, this strategy is constrained by the event of agglomeration amid the washing, separating, and drying stages. The size and state of the nanoparticles created utilizing this technique are subject to the following: sort of salt utilized (chlorides, sulfates, nitrates, perchlorates, and so forth), proportion of ferric and ferrous particles, response temperature, arrangement pH, ionic quality of the media, and other response factors (mixing rate, method of arrangement expansion, and so forth).

7.7.3 Hydrothermal Method

An elective method for incorporating magnetite is by the hydrothermal method. Aqueous combination is done under high temperature and weight in an autoclave with water as the response medium, advancing disintegration and response of typically sparingly solvent and insoluble substances followed by side-effect recrystallization. Both high temperature and high weight offer a few advantages, including change in attractive property and item immaculateness. Aqueous union can likewise adequately control the size and state of particles and limits molecule agglomeration. In this manner, the technique is fit for creating particles with great dispersibility and uniform size. The technique should be possible either with or without the utilization of particular surfactants.

7.7.4 Characteristics of Magnetic Adsorbents

The synthetic and physical properties, particularly the magnetic properties, of magnetic adsorbents characterize their expected applications in ecological, scientific, compound, and dye extraction enterprises. These qualities are exceedingly reliant on properties, for example, molecule size, morphology, precious stone structure, and the surface useful gatherings of the readied adsorbents. There are a huge number of portrayal procedures accessible these days to decide these highlights. This segment portrays the most well-known and broadly utilized ones.

7.8 Conclusion

Magnetism of the adsobents is a special property that self-governingly aids water/wastewater cleaning by affecting the physical properties of contaminants in watery arrangements. In this way, magnetic detachments of toxins have been utilized broadly in wastewater treatment and natural cleanup. Magnetic adsorbents are promising contenders for bigger scale wastewater treatment because of their simple functionalization, minimal effort, high adsorption limit, solid physicochemical security, and simple partitions. In this manner, these adsorbents can be proficiently used for the treatment of wastewater containing perilous dyes and lethal metal particles.

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Chapter 8
Date Palm as a Potential Candidate for Environmental Remediation

Jaskiran Kaur

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Abstract The water bodies are under continuous stress conditions owing to water pollution, and this problem is increasing continuously in line with industrialization. Consequently, utmost attention is needed to embark upon pollution problems so as to fulfil the dream of sustainable development. In the present era, adsorption has been considered as an efficient method for the removal of suspended and dissolved pollutants from the water resources. It has been confirmed that among the various types of bioadsorbents, date palm emerged as a highly cost-efficient and biodegradable bioadsorbent. A number of recent reports signified the role of date palm as a bioadsorbent. The present review is exploring the use of different by-products of date palm as adsorbent as well as a precursor to activated carbon production. Herein, an in-depth analysis of the role of date palm in the environmental remediation, in terms of removal of different pollutants, viz. dyes, heavy metals and toxins, has been examined.

Keywords Industrialization · Water pollution · Adsorption · Date palms · Adsorption characteristics

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J. Kaur (✉)
Department of Environmental Science and Technology, School of Environment and Earth Sciences, Central University of Punjab, Bathinda, India

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8.1 Introduction

Over the past few decades, the industrial revolution plays an instrumental role in the economic growth and prosperity of the country. But, with the rapid expansion of industries, an enormous pressure is exerted on the environment. It turned out that the residence of environmental contaminants in environmental media, viz. round water, surface water soil and sediments, poses a serious threat to the environment and human health (Ghasemi et al. 2014; Naushad et al. 2016a). Subsequently, the impacts on water resources seem to be more severe which cannot be overlooked. The problem of massive water pollution is demarcated as the consequence of the discharge of industrial wastewater into the water bodies. As a matter of fact, billions of tons of wastewater are generated by industries every year (Sagasta et al. 2015).

The wastewater discharged as such into the rivers, lakes and streams results in health hazards such as eye irritation, skin and neurological problems, degenerative heart disease, gastroenteritis, blue baby syndrome, typhoid fever, shigellosis, salmonellosis, campylobacteriosis, cholera, giardiasis, cryptosporidiosis and hepatitis A and liver cancer in animals (Eynard et al. 2000; Mahmood and Maqbool 2006; Akpor and Muchie 2011). In addition, wastewater effluents are accountable for ruining the quality of receiving water bodies resulting in problems of eutrophication of water bodies, biomagnification in the aquatic life and decreased dissolved oxygen (Welch 1992; Akpor and Muchie 2011). These problems are getting grimmer day by day. So, in order to protect the receiving waters from these obnoxious effects, specialized treatments are needed.

The researcher's works around the clock to develop methods for tackling these profound effects of industrial pollutants are continuously going on. An array of technologies are available for the pollutants remediation, such as advanced oxidation, ozonation, chemical precipitation, ion exchange, coagulation, flocculation, electrodialysis, ultrasonic treatment, reverse osmosis, membrane filtration, solvent extraction and adsorption (Abdulkarim et al. 2002; Al-Ghouti et al. 2010; Bhattacharyya and Gupta 2008; Bratskaya et al. 2009; Chang et al. 2009; El Samrani et al. 2008; Hall et al. 1990; Ku and Jung 2001; Landaburu-Aguirre et al. 2010; Mohsen-Nia et al. 2007; Murthy and Chaudhari 2008; Nataraj et al. 2007; Ostroski et al. 2009; Suzuki et al. 2000; Terry 2010; Al-Othman et al. 2012; Mittal et al. 2016; Naushad and ALOthman 2015; Alqadami et al. 2017; Albadarin et al. 2017). But, many of these technologies are ineffective because of the shortcomings of generation of toxic fumes during chemical precipitation, high power consumption in reverse osmosis method, secondary pollution problem during ion-exchange method, increase sludge volume generation in coagulation/flocculation and membrane fouling during membrane filtration (Dialynas and Diamadopoulos 2009; Fu and Wang 2011; Shafiq et al. 2018). The adsorption process is considered a vivid remediation technology owing to its simplicity, reliability and low maintenance cost. Activated carbon holds a significant promise as an efficient adsorbent for pollutant removal (Ahmad et al. 2012; Naushad et al. 2016b). However, in spite of its high adsorption nature and maximum porous surface area, the problem of high cost of production has inclined the researchers towards the development of low-cost adsorbents.

Date palm is one such low-cost adsorbent which have been extensively used throughout the world for removal of various types of pollutants. In this review, the research advances in the use of date palm for removal of various wastewater pollutants as well as its role in phytoextraction have been documented.

8.2 Chemical Composition and Properties of Date Palm

Date palm known as *Phoenix dactylifera* L. scientifically is one of the major commercially growing crops in Middle East Asia and North Africa (Ahmad et al. 2012). Its global production has observed to be around 7.68 million tons in 2010 (Tang et al. 2013). As far as regional distribution is concerned, it has been seen that around 60 million date palm trees are cultivated in Asia (for instance, Iran, Saudi Arabia, Kuwait, Bahrain, Turkmenistan, UAE, Iraq, Pakistan, Oman and Yemen) and approximately 32.5 million date palm are grown in Libya, Algeria, Mali, Egypt, Mauritania, Morocco and Niger countries of Africa region (Jamil et al. 2016; Shafiq et al. 2018). Besides being used as a fruit, date palm and its products are used for the purpose of pollutant removal over the centuries which are attributable to its chemical composition.

Indeed the chemical study of date palm revealed that it consists of cellulose (40–50%), hemicellulose (20–35%) and lignin (15–35%) as major components along with some minor components such as oil and proteins (Macedo et al. 2008). Cellulose is a crystalline polysaccharide consisting of a linear chain of up to 3000 β(1→4) linked D-glucose units. Hemicellulose though related to cellulose is unbranched and contains a lesser number of saccharide units compared to that of cellulose. The third major component, i.e. lignin, can contribute significantly to the adsorption property of date palm. Structurally, it contains complex and variable constituents. The three polypropylene units are present in its structure which are linked together by ether linkages (C–O–C) and carbon–carbon bonding (C–C). Therefore, its elemental composition has higher carbon percentage of around 62 wt% and lower oxygen percentage of 32 wt%. The presence of a large number of carbon atoms is commonly linked with a lower polarity and thus a better prospect for adsorption. As a consequence, the date palm is an ideal adsorbent for adsorption practices (Jibril et al. 2008).

8.3 Role of Date Palm in Environmental Remediation

Environmental remediation aims to reduce harmful substance exposure from groundwater, surface water and contaminated soil. To help with the remediation of affected sites, date palm has been widely explored as an adsorbent by researchers all around the world. Figure 8.1 depicts the role of date palm as an adsorbent in the removal of various industrial pollutants such as heavy metals, phenols, dyes as well as in phytoextraction.

Fig. 8.1 Contribution of date palm in environmental remediation

8.3.1 Removal of Heavy Metals

Contamination of water bodies by heavy metals is of serious environmental concern. Industries such as pulp and paper, tannery, mining, electroplating, smelting and textiles generate substantial amounts of heavy metals from wastewater which is discharged into the rivers and streams. Above their threshold limits, they tend to accumulate in the food chain, causing neurological disorders, cancer and accumulative poisoning (Abdulkarim and Al-Rub 2004; Al-Jlil 2010). Since the toxicity of heavy metals is one of the severe health issues for decades, therefore, efficacious recovery of heavy metals from the water bodies is the need of the time (Naushad et al. 2017). Date palm and its by-products have been investigated as a preferred solution towards removal of these toxic heavy metals by various researchers (Haleem and Abdulgafoor 2010; Al-Haidary et al. 2011).

Al-Jlil (2010) investigated the removal of various heavy metals such as Cr, Co, Cu, Zn, As, Pb and Cd from industrial wastewater by roasted date pits. The results revealed that the heavy metal concentration from industrial wastewater treated with roasted date pits was less than the permissible limits for crop production compared to untreated wastewater except for the Co ion whose concentration was observed to be two times higher than the permissible limits. However, the absence of Co ion was seen when roasted date pits are used in series with other adsorbents, i.e. bentonite clay.

The extent of adsorption of heavy metals is controlled by a number of factors such as contact time, pH, a dosage of the adsorbent, particle sizes, initial metal concentration and temperature. In a study by Al-Haidary et al. (2011), the adsorption of Pb from aqueous solution by date palm fibres and leaf base of palm (petiole) was examined by considering the effect of numerous parameters, for instance, contact time, solution pH, adsorbent dosage, particle sizes of date palm materials, ionic strength and temperature. An increase in adsorption of Pb ions was observed with increase in adsorbent dosage as well as with the increase in contact time. An increase in adsorbent dosage could result in an increase in the surface area, thereby providing more binding sites for adsorption. The linear Langmuir and Freundlich models were used to comprehend the adsorbate-adsorbent interaction. Based on Langmuir isotherm, the adsorption capacity of Pb ion onto date palm fibres and petiole was calculated as 18.622 and 20.040 mg/g, respectively. The pseudo-second-order kinetics model correlated well with the adsorption kinetics of Pb ion from aqueous solution onto palm fibres and petiole. In another study of heavy metal, i.e. Cu removal by date palm from aqueous solutions conducted by Belala et al. (2011a), the effect of adsorbent particle size on removal efficiency was examined. The authors concluded that the removal efficiency was highest with adsorbent particles of small size. Maximum efficiency was in the range between 60% and 80% with the adsorbent particle size below 1 mm. Further, the study performed by Al-Ghamdi et al. (2013) indicated that the adsorption of heavy metal Cd^{2+} increased to 51.1 mg/g from 29.06 mg/g with the decrease in particle size from 875 to 100 μm. However, increasing the solution pH from 1.69 to 3.71 resulted in an increase in adsorption capacity.

Besides being used as an adsorbent, the carbon-rich raw date palm can also be used for the preparation of activated carbon which has been extensively used as adsorbent material for removal of a variety of contaminants. The ability of date palm derived activated carbon to adsorb heavy metals from aqueous metal solutions and wastewater has been reported in several studies (Banat et al. 2003a; Hilal et al. 2012; Chaouch et al. 2013, 2014; Nwakonobi et al. 2018).

El Nemr et al. (2008) prepared activated carbon from date palm seed by dehydrating approaches using concentrated sulfuric acid for removal of Cr(VI) from aqueous solution. The results showed that adsorption capacity increases with a decrease in pH value. The maximum adsorption capacity reported was 120.48 mg/g. Nwakonobi et al. (2018) used activated carbon prepared from the date palm seeds for removal of heavy metals, viz. Pb, Cr and Cd, from brewery wastewater. The adsorption experiments were carried out in batch studies under conditions such as contact time and adsorbent dosage. It has been concluded that at 60 min of contact time, different adsorbent doses of 10×10^3, 20×10^3, 30×10^3 and 40×10^3 mg/L reduced the Cr and Pb concentration below the World Health Organization (WHO) maximum limits of 0.05 and 0.01 mg/L, respectively. Cd concentration was brought within WHO maximum limit (0.003 mg/L) using 30×10^3 mg/L of the adsorbent at 80 min of contact time. A summary of adsorption of different metal ions by date palm-based adsorbents is presented in Table 8.1.

Table 8.1 Removal of heavy metals from water and wastewater by date palm

Adsorbent used	Heavy metals to be removed	Source of heavy metal	Conditions employed	Adsorption capacity	Removal efficiency	References
Date palm and its by-products						
Raw date pits	Zn (II)	Aqueous solutions	pH—3.5 to 5.0 Contact time—2 to 8 h Temperature—25, 40 and 50 °C	5.70 mg/g	–	Banat et al. (2002)
Raw date pits	Cu (II)	Aqueous solutions	pH—3.5 to 5.0 Contact time—2 to 8 h Temperature—25, 40 and 50 °C	9.53 mg/g	–	
Date pits	Cd (II)	Aqueous solutions	pH—2 to 7 Contact time—24 h Temperature—25, 35 and 45 °C	6.5 mg/g	–	Banat et al. (2003a)
Date palm fibres (leaf)	Cr (VI)	Aqueous solutions	pH—7 Biosorbent dose—5 g Contact time—48 h	–	98.7%	Haleem and Abdulgafoor (2010)
Raw date pits	Cu (II)	Aqueous solutions	pH—2 to 11 Contact time—72 h Temperature—20 °C	35.9 mg/g	–	Al-Ghouti et al. (2010)
Raw date pits	Cd (II)	Aqueous solutions	pH—2 to 11 Contact time—72 h Temperature—20 °C	39.5 mg/g	–	

Roasted date pits	Zn	Industrial wastewater	pH—7.67 Temperature—25 °C	–	97%	Al-Jlil (2010)
Roasted date pits	Co	Industrial wastewater	pH—7.67 Temperature—25 °C	–	97%	
Roasted date pits	Cd	Industrial wastewater	pH—7.67 Temperature—25 °C	–	97%	
Roasted date pits	Cr	Industrial wastewater	pH—7.67 Temperature—25 °C	–	97%	
Roasted date pits	As	Industrial wastewater	pH—7.67 Temperature—25 °C	–	97%	
Roasted date pits	Pb	Industrial wastewater	pH—7.67 Temperature—25 °C	–	97%	
Raw date pits	Cu (II)	Aqueous solution	pH—2.1 to 9.05 Adsorbent dose—0.01 to 2 g/L Contact time—200 min Temperature—25 ± 1 °C	7.40 mg/g	–	Hilal et al. (2012)
Raw date pits	Cd (II)	Aqueous solution	pH—2.1 to 9.05 Adsorbent dose—0.01 to 2 g/L Contact time—200 min Temperature—25 ± 1 °C	6.02 mg/g	–	

(continued)

Table 8.1 (continued)

Adsorbent used	Heavy metals to be removed	Source of heavy metal	Conditions employed	Adsorption capacity	Removal efficiency	References
Date palm trunk and leaves	Cu (II)	Aqueous solutions	pH—5 to 10 Contact time—15 to 180 min Temperature—30 to 50 °C	39.6 mg/g	–	Amin et al. (2017)
Date palm trunk and leaves	Pb (II)	Aqueous solutions	pH—5 to 10 Contact time—15 to 180 min Temperature—30 to 50 °C	30 mg/g	94%	
Date palm trunk and leaves	As (V)	Aqueous solutions	pH—5 to 10 Contact time—15 to 180 min Temperature—30 to 50 °C	25 mg/g	63%	
Date seed-derived biochar	Ni (II)	Aqueous solutions	pH—2 to 6 Temperature—23 ± 2 °C	35.7 mg/g	–	Mahdi et al. (2017)
Date seed-derived biochar	Pb (II)	Aqueous solutions	pH—2 to 6 Temperature—23 ± 2 °C Contact time—24 h	74.6 mg/g	–	Mahdi et al. (2018)
Date pits as a precursor of activated carbon						
Activated date pits	Zn (II)	Aqueous solution	pH—3.5 to 5.0 Contact time—2 to 8 h Temperature—25, 40 and 50 °C	5.23 mg/g	–	Banat et al. (2002)
Activated date pits	Cu (II)	Aqueous solution	pH—3.5 to 5.0 Contact time—2 to 8 h Temperature—25, 40 and 50 °C	8.89 mg/g	–	

Carbonized date pits (500 °C)	Cd (II)	Aqueous solution	pH—2 to 7	3.0 mg/g	–	Banat et al. (2003a)
			Contact time—24 h			
			Temperature—25, 35 and 45 °C			
Carbonized date pits (900 °C)	Cd (II)	Aqueous solutions	pH—2 to 7	1.8 mg/g	–	
			Contact time—24 h			
			Temperature—25, 35 and 45 °C			
Date stone activated carbon	Zn (II)	Aqueous solutions	pH—6	10.41 mg/g	–	Mouni et al. (2010)
			Adsorbent dose—0.2 to 10.0 g/dm			
			Contact time—1 h			
			Temperature—20 °C			
Date stone activated carbon	Pb (II)	Aqueous solutions	pH—6	19.64 mg/g	–	
			Adsorbent dose—0.2 to 10.0 g/dm			
			Contact time—1 h			
			Temperature—20 °C			
Activated date pits	Cu (II)	Aqueous solutions	pH—2.1 to 9.05	33.44 mg/g	–	Hilal et al. (2012)
			Adsorbent dose—0.01 to 2 g/L			
			Contact time—200 min			
			Temperature—25 ± 1 °C			
Activated date pits	Cd (II)	Aqueous solutions	pH—2.1 to 9.05	17.24 mg/g	–	
			Adsorbent dose—0.01 to 2 g/L			
			Contact time—200 min			
			Temperature—25 ± 1 °C			
Date stone activated carbon	Pb (II)	Aqueous solutions	pH—2 to 10	11.8 mg/g	–	Chaouch et al. (2014)
			Contact time—2 h			
			Temperature—25 to 60 °C			

(continued)

Table 8.1 (continued)

Adsorbent used	Heavy metals to be removed	Source of heavy metal	Conditions employed	Adsorption capacity	Removal efficiency	References
Mercerized mesoporous date pit activated carbon	Cd (II)	Aqueous solutions	pH—1 to 9	212.1 mg/g	–	Aldawsari et al. (2017)
			Contact time—1 to 1440 min			
			Temperature—298 K			
Mercerized mesoporous date pit activated carbon	Cu (II)	Aqueous solutions	pH—1 to 9	194.4 mg/g	–	
			Contact time—1 to 1440 min			
			Temperature—298 K			
Mercerized mesoporous date pit activated carbon	Pb (II)	Aqueous solutions	pH—1 to 9	133.5 mg/g	–	
			Contact time—1 to 1440 min			
			Temperature—298 K			
Mercerized mesoporous date pit activated carbon	Zn (II)	Aqueous solutions	pH—1 to 9	111 mg/g	–	
			Contact time—1 to 1440 min			
			Temperature—298 K			

sizes (1.47, 0.8, 0.45 and 0.225 mm) of adsorbent were used for this study. The data of the adsorption kinetics of phenol exhibited a good fit with the pseudo-second-order kinetic equation.

8.3.3 Dye Removal

Dyes are coloured compounds used extensively by textile, tannery, paper, plastic, cosmetics, leather, food and pharmaceutical industries. It is estimated that worldwide over the year, around 7×10^5 tons of synthetic dyes are produced, 10% of which are discharged in the effluent during dyeing operations while 1–2% are known to lose in the effluent during manufacturing operations (Garg et al. 2004). As dyes are toxic and carcinogenic, so such dye-contaminated effluent when discharged into the natural receptor water could make water toxic to aquatic life. In addition, it has been reported that exposure to dye effluent may cause problems such as skin irritation, sore eyes, increased heart rate, jaundice carcinogenicity, chromosomal fractures and respiratory toxicity in humans (Papic et al. 2000; Ahmad and Alrozi 2011). Therefore, it is environmentally imperative to decrease the concentration of dyes in the wastewater before discharging it into the water bodies. Adsorption of dyes onto the date palm has been reported in the literature as a predominately accepted method for removal of different types of dyes including methylene blue, malachite green, crystal violet, eosin, acid black, etc. (Banat et al. 2003b, Belhachemi et al. 2009; Mahmoodi et al. 2010; Alshabanat et al. 2013; Alshabanat et al. 2016; Alzahrani and El-Mouhty 2016).

Table 8.2 summarizes a non-exhaustive list of studies related to the use of date palm and its by-products as well as activated carbon derived date palm for different dye removal. In particular, a study by Belala et al. (2011b) explored the biosorption of methylene blue from aqueous solution by date stones and palm trees waste. The maximum biosorption capacities obtained with date stones and palm trees waste for methylene blue were 43.5 and 39.5 mg/g, respectively. The authors also evaluate the experimental data through kinetic models. Results revealed the involvement of pseudo-second-order kinetics behind the adsorption of methylene blue on to palm trees waste and date stones.

Banat et al. (2003c) impregnated the raw date pits with 30% (wt.) KOH solution prior to carbonization (for 2 h at 600 ° C) and CO_2 activation (for 1 h at 800 ° C) in order to study the effect of chemically activated date pits towards removal of methylene blue. An increase in adsorption capacity from 80.3 mg/g to 123.1 mg/g was observed upon chemical activation. The results were found to be opposite to that obtained during physical activation by Banat et al. (2003b). They reported a decrease in adsorption capacity from 80.3 mg/g to 12.9 mg/g and to 17.3 mg/g during activation of date pits at 500 °C and 900 °C, respectively. This points out that the uptake of dye by the activated carbon is not merely controlled by the surface area but also by the pore-size distribution and the adsorbent's surface chemistry.

Table 8.2 Summary of the removal of various dyes by the date palm

Adsorbent used	Pollutants to be removed	Conditions employed	Adsorption capacity	References
Date fruit pits activated carbon	Methylene blue	Adsorbent dose—0.25 g Contact time—48 h Temperature—25 °C	590 mg/g	Abdulkarim et al. (2002)
Raw date pits	Methylene blue	pH—4 to 8 Adsorbent dose—6 mg/mL Contact time—24 h Temperature—25 to 50 °C	80.3 mg/g	Banat et al. (2003b)
Activated date pits (500 °C)	Methylene blue	pH—4 to 8 Adsorbent dose—6 mg/mL Contact time—24 h Temperature—25 to 5	12.9 mg/g	
Activated date pits (900 °C)	Methylene blue	pH—4 to 8 Adsorbent dose—6 mg/mL Contact time—24 h Temperature—25 to 5	17.3 mg/g	
Date stone activated carbon	Methylene blue	Contact time—20 h Temperature—room temperature	148 mg/g	Alhamed (2006)
Date pits activated carbon	Methylene blue	Adsorbent dose—0.2 g Contact time—36 h Temperature—25 °C	127.3 mg/g	El-Sharkawy et al. (2007)
Chemically modified date pits activated carbon	Methylene blue	Adsorbent dose—10 mg Temperature—25 °C	216.4 mg/g	Belhachemi et al. (2009)
Date stone	Acid green 25	pH—2 to 12 Adsorbent dose—1 to 3 g/L Contact time—30 min Temperature—25 to 65 °C	36.496 mg/g	Mahmoodi et al. (2010)
Date stone	Acid black 26	pH—2 to 12 Adsorbent dose—1 to 3 g/L Contact time—30 min Temperature—25 to 65 °C	39.526 mg/g	
Date stone	Acid blue 7	pH—2 to 12 Adsorbent dosage—1 to 3 g/L Contact time—30 min Temperature—25 to 65 °C	33.784 mg/g	
Raw date pits	Methylene blue	pH—4 to 10 Contact time—72 h Temperature—20 °C	277.8 mg/g	Al-Ghouti et al. (2010)

(continued)

Table 8.2 (continued)

Adsorbent used	Pollutants to be removed	Conditions employed	Adsorption capacity	References
Date palm fibre	Crystal violet	pH—2 to 11 Temperature—25 to 55 °C °C	0.66 × 10^{-6} Mol/g	Alshabanat et al. (2013)
Date palm fibres	Malachite green	pH—4 to 10 Temperature—25 to 45 °C	0.2136 Mol/g	Alshabanat et al. (2016)
Date palm trunk-derived activated carbon	Eosin dye	pH—1 to 11 Adsorbent dose—0.2 to 1 g Contact time—5 to 50 min Temperature—25 °C	126.58 mg/g	Alzahrani and El-Mouhty (2016)
Date palm fibres	Methylene blue	pH—2 to 10 Adsorbent dose—50 to 250 mg Contact time—20 min Temperature—25 ± 0.5 °C	4.554 mg/g	Shagufta et al. (2018)

8.3.2 Hazardous Materials Removal

Phenol is regarded as one of the noxious pollutants found in the wastewater of ceramic, steel, petrochemical, oil, pharmaceutical, chemical and fertilizer industries (Aksu and Yener 2001). The presence of phenol in water bodies even at low concentration can cause chronic toxic effects. So, to remove phenol from the aqueous solution, adsorption onto the low-cost adsorbent such as date palm is widely employed. Banat et al. (2004) while investigating the adsorption of phenol onto raw and activated date pits concluded that activated date pits had 16 times higher adsorptive capacity compared to raw date pits. Thermodynamic parameters studied showed that the dye removal through adsorption was endothermic. Furthermore, an increase in phenol uptake by activated carbon was observed with an increase in initial phenol concentration from 10 to 200 ppm and temperature from 25 °C to 55 °C. While with an increase in solution pH (from 4 to 12), a decrease in phenol adsorption was noted. However, in a study by Mane et al. (2005), a decrease in the amount of phenol adsorption from 33.12 mg/g to 24.10 mg/g was observed with an increase in temperature from 30 to 60 °C. This indicated the exothermic nature of the reaction.

The research conducted by Abdulkarim et al. (2002) evaluated the phenol adsorption onto the date fruit pit prepared activated carbon. The results showed the high adsorption capacity of activated carbon for phenol, 2-nitrophenol and 2,4- and 2,4,6-trinitrophenol. Moreover, the experimental data for adsorption of phenols were found to fit both the Freundlich and Langmuir isotherms. Alhamed (2009) investigated the adsorption kinetics and performance of packed bed adsorbent for phenol removal using dates stones prepared activated carbon. Four different particle

A comparative study of the removal of methylene blue by adsorption and photocatalytic degradation was reported by El-Sharkawy et al. (2007). Two types of activated carbon – steam-activated carbons and $ZnCl_2$-activated carbons – were prepared from date pits. Among these two, the steam activated carbon was considered more efficient in the methylene blue dye decolourization. The higher surface area, the total pore volume and the basic nature of the surface are responsible for the better decolourization ability of steam activated carbon. Further, when the removal of methylene blue via adsorption and photocatalytic degradation was compared, it can be seen that with photocatalytic degradation, the complete removal of the dye occurs within 10–22 h. On the other hand, the methylene blue adsorbed on the activated carbon might not easily be recovered which therefore contribute to environmental pollution.

As apparent from the literature review, the date palm and its derived activated carbon is highly efficient in removal of methylene blue dye, but its adsorption capacity is not only limited to methylene blue (Table 8.2). The aqueous solutions contaminated with other dyes, for instance, crystal violet, malachite green, eosin and many more, could also be treated through the application of date palm. For example, in a study by Sulyman et al. (2016), adsorptive removal of crystal violet by date palm dead leaflets derived activated carbon was investigated. The equilibrium adsorption of crystal violet was determined under different initial dye concentration, pH contact time and adsorbent dose. The maximum adsorption capacity of date palm dead leaflets derived activated carbon was about 36.63 mg/g. In addition, it was found that dye removal increased with the increase in pH, adsorbent dose and contact time. Also, the isotherm equilibrium was well fitted by the Langmuir and Freundlich models.

8.3.4 Role in Phytoextraction

The content of heavy metals including chromium, copper, cadmium, arsenic, lead, zinc and nickel has increased continuously in the soil as a result of industrial activities. The presence of heavy metals in high concentrations not only inhibits the plant metabolic functions including physiological and biochemical processes, water absorption, photosynthesis, respiration, mitosis and plant's cell organelles degeneration but also affects the size, composition and activity of soil microbes (Yao et al. 2003; Bhattacharyya et al. 2008).

The remediation of heavy metals from the contaminated soil through the phytoextraction method is now receiving research attention. Phytoextraction is one of the subprocesses of phytoremediation which encompasses the use of plants for the extraction of heavy metals from the contaminated soil. Date palms, however, are known to play an indispensable role in phytoextraction process. A huge number of studies have focused on the intercropping of various plant species with date palm for the removal of heavy metals (Hamid 2011; Mohebbi et al. 2012).

Hamid (2011) conducted an experiment to study the possibilities of remediation of heavy metals from the contaminated soil by alfalfa, maize and sunflower grown with and without date palm. He found that monoculture of sunflower had a significantly higher ability of cadmium uptake than alfalfa and corn. The copper and manganese uptake index was found to be higher in the monoculture of corn. Thus it can be seen that intercropping with date palm did not show a significant effect on the accumulation and removal of heavy metals. However, in another study by Mohebbi et al. (2012) on phytoextraction of heavy metals by corn, alfalfa and sunflower grown in monoculture and intercropping with date palm, it can be seen that date palm-intercropped sunflower has high biological concentration factor (BCF) values for Mn and Cu among other crops. The high value of BCF indicated retention of metals in roots thereby results in limiting the mobility of metals from roots to shoots.

Mohebbi (2012) in his study showed that Cu concentration in roots and shoots of corn, alfalfa and sunflower grown with and without date palm was more than 21 and 14 mg/kg, respectively. He concluded that among these three crops, the crop alfalfa exhibited the highest translocation factor when co-planted with date palm. On the contrary, higher translocation factor was recorded in monocropped sunflower compared to date palm co-planted sunflower.

8.4 Conclusion and Future Perspectives

Date palm which is known for its nutritional value has been proven to have considerable potential to remove the harmful substances from the wastewaters. As reported in the literature, the low-cost date palm has considered being a successful replacement for expensive activated carbon. This review is an attempt to cover the different areas where the date palm has been successfully used. Time and again, raw date palm and its by-products were tested as an adsorbent for effectual removal of various pollutants. However, different experimental conditions, such as solution pH, initial dye concentration, adsorbent dosage, contact time and temperature of the system, need to be taken into account during evaluation of the adsorptive capacity of date palm. Since, most of the studies revealed the pollutant removal from aqueous solution, hence, further study is needed to evaluate the pollutant removal from real wastewater. In addition, the actual mechanism behind the interaction between the adsorbent and the pollutant still requires detailed research.

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Chapter 9
Research Updates on Heavy Metal Phytoremediation: Enhancements, Efficient Post-harvesting Strategies and Economic Opportunities

S. Muthusaravanan, N. Sivarajasekar, J. S. Vivek, S. Vasudha Priyadharshini, T. Paramasivan, Nirajan Dhakal, and Mu. Naushad

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S. Muthusaravanan · N. Sivarajasekar (✉) · J. S. Vivek · S. Vasudha Priyadharshini
T. Paramasivan
Laboratory for Bioremediation Research, Unit Operations Laboratory, Department of Biotechnology, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India

N. Dhakal
Environmental Engineering and Water Technology Department,
IHE Delft Institute for Water Education, Delft, The Netherlands

M. Naushad
Department of Chemistry, College of Science, King Saud University, Riyadh, Saudi Arabia

M. Naushad, E. Lichtfouse (eds.), *Green Materials for Wastewater Treatment*,
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Abstract The remediation of heavy metal-contaminated sites must be viewed seriously as they affect the animal and human health. The amount of heavy metal released from the industries into the environment is expected to be more in the future due to rapid urbanization, industrialization, increased population and war spoil. The plant-mediated remediation of heavy metals from the contaminated site known as 'phytoremediation' was found to be effective, economically viable and safe. In this review, we elaborate the effect of heavy metal on human health, mechanisms of metal uptake in plants, enhancement techniques and challenges in the implementation of phytoremediation, comparison of existing physiochemical methods available for heavy metal with phytoremediation and disposal of metal-contaminated plant biomass in the economically profitable ways.

Keywords Heavy metals · Phytoremediation · Mechanisms · Challenges · Disposal · Economy

Abbreviations

CDTA	Cyclohexane-1,2-diamine tetra-acetic acid
CNS	Central nervous system
DMA	Dimethyl arsenic acid
DTPA	Diethylenetriaminepentaacetic acid
EDDS	Ethylenediamine-*N*, *N*′-disuccinic acid
EDTA	Ethylene diamine tetra-acetic acid
EDX	Energy-dispersive X-ray spectroscopy
EGTA	Ethylene glycol-bis-(beta-amino-ethyl ether) *N*, *N*, *N*′, *N*′-tetra-acetic acid
GI	Gastrointestinal
HMCB	Heavy metal-contaminated biomass
MMA	Monomethyl arsenic acid
NTA	Nitrilotriacetic acid

TEM	Transmission electron microscopy
UV	Ultraviolet
XRD	X-ray diffraction

9.1 Introduction

Due to urbanization, mining, manufacturing and ammunition, the ecosystem has become increasingly contaminated by organic and inorganic contaminants (Nabi and Naushad 2007). The soil becomes contaminated by these pollutants released from industries and creates health issues in different life forms. Among the all known contaminants, heavy metals play an important role in polluting the ecosystems on a large scale (Nabi and Naushad 2010). Heavy metals are posing a serious threat to humanity as they are extremely toxic and have the ability to enter the food chain (Muthusaravanan et al. 2018). Heavy metal contaminations are hard to remediate due to its structural properties. They persist in the environment for a longer duration after ingestion as they are non-biodegradable, and hence, their accumulation improves their toxicity levels significantly (Khan et al. 2009a, b). Heavy metals are easily dispersible through air and water so there is a higher chance of transfer around the vicinity area around the polluted site (Neilson and Rajakaruna 2012). Heavy metal contamination is now becoming threat, and many countries are looking for a cost-effective remedy (Naushad et al. 2015).

Some of the reported issues regarding heavy metal contamination are:

- Nickel contamination in the waste waters from five different ghee industries in Pakistan was reported by Khan et al. (2009a, b).
- The high concentration of heavy metals Cd, Cu, Zn and Pb was found in tubers grown in and around Copsa Mica and Baia Mare in Romania (Lăcătuşu et al. 1996).
- Japan designated three heavy metals Cu, Cd and As as toxic under Agricultural Land Soil Pollution Prevention Law (1970) as the country suffered heavy contamination in their agricultural lands in the past (Arao et al. 2010).
- Heavy metals particularly Cd and Pb were found in vegetables grown in regions of Boolaroo and Port Kembla near the vicinity of smelters in Australia (Kachenko and Singh 2006).
- Feng County in China has faced issues with the contamination of zinc due to the mineral industrial process and acute environmental pollution accidents from the emissions by smelters and mining processing wastes over the past 30 years (Awasthi et al. 2017).

The maximum permissible levels for some heavy metal designated by WHO (World Health Organization) are listed in Table 9.1.

The accumulation of heavy metals above the given permissible levels will cause adverse effects in the human body (Naushad and AlOthman 2015; Schober et al. 2006). With the alarming effects, there is a need for the regulation of heavy metals

Table 9.1 The permissible heavy metal concentration in drinking water as designated by WHO guideline

Heavy metals	Max. acceptable concentration (mg/L) from WHO
Zinc	5
Arsenic	0.01
Cadmium	0.003
Lead	0.01
Silver	0
Mercury	0.001
Copper	1.3
Nickel	0
Chromium	0.1

in soil and water so that the adverse effects on human and animal biota could be limited (Gutha et al. 2015). In the last two decades, different technologies have emerged to remediate the contaminated lands, and those are classified into physicochemical remediation and bioremediation (Chaney et al. 1997). The physicochemical remediation includes vapour extraction, incineration, solidification, thermal desorption, soil leaching, adsorption, ion exchange, etc. (Al-Othman et al. 2011; Alam et al. 2013; Nabi et al. 2009). But these methods are costly and have limitations to practice (Caliman et al. 2011). On the other hand, bioremediation techniques such as microbial remediation, plant-mediated remediation, etc. play an important role in wasteland remediation in an economically viable way. Phytoremediation is the type of bioremediation where plants were utilized to clean up the contaminated sites being a popular option for the remediation of contaminated sites in the last decades due to their increased efficiency, low cost and suitability for both in situ and ex situ mode of operation (Khan et al. 2000).

Although phytoremediation has good potential for remediating heavy metal-contaminated sites, there are few limitations which made this technology a controversial one. One such limitation is disposal of metal-contaminated plant residues after remediating the contaminated site. During the last decade, scientists proposed numerous techniques for safe disposal of metal-contaminated biomass such as composting, compaction, combustion and gasification. The composting and compaction only limit the movement of the residues and prevent it from entering into the biotic cycle, whereas combustion and gasification generate metal-containing ashes and harmful gases during the process. Later on, the metal-containing biomass collected from the remediated sites was converted into various commercial valuable products using modern technologies.

In this review, we focused on the effect of heavy metals on the biotic system, mechanisms involved in phytoremediation of heavy metals, need for phytoremediation, potential challenges, enhancement processes and methods for disposal of metal-contaminated biomass, and economic opportunity for biomass remains.

9.2 Heavy Metals and Its Effects on Human and Animal Health

Serious complications in both human and animals have been reported due to exposure of heavy metals since these metals bind to the biologically important protein and replacing them, resulting in functional loss and cellular disintegration. Some metals are also found to be carcinogenic when they interact with the nucleic acid or nuclear proteins induce oxidative stress and results in cell damage. Some heavy metals and their effect on the human health were elaborated below.

9.2.1 Arsenic

Arsenic is a heavy metal widely used in synthetic fertilizers, pesticides and for a wide range of industrial applications (Cullen and Reimer 2016). Harmful inorganic arsenic compounds such as monomethyl arsenic acid (MMA) and dimethyl arsenic acid (DMA) are produced by bacteria, algae, fungi and humans (Council NR 1999). Methylated MMA (V) and DMA (V) were excreted through urine, but MMA (III) which could not be excreted persists within the cell. MMA (III) is found to be highly toxic compared to other arsenic derivatives and leads to many health issues (Jomova et al. 2011).

9.2.2 Lead

Lead is an extremely poisonous metal whose distributed use has caused large environmental contamination and health-related problems in many regions of the globe (Raistrick and Jennings 1965; Naushad and ALOthman 2015). Lead metal induces toxicity in living cells by tailing ionic mechanism and results in oxidative stress. Previous studies have shown that lead causes oxidative stress in living cells by promoting imbalance between the free radicals produced and antioxidants generated to counteract and repair the resulting damage. Pb contamination in agricultural lands may result in severe environmental problems such as loss of vegetation, decreased soil fertility, groundwater contamination and bioaccumulation in living systems (Flora et al. 2012).

9.2.3 Mercury

Mercury is very toxic and exceedingly bioaccumulative. Its presence widely affects both terrestrial and marine environment, and hence, many researches are focused towards the monitoring of the presence of mercury in land and aquatic environment and to remediate the Hg-contaminated sites (Snyder 1971). The chronic or prolonged exposure to elemental Hg can lead to its accumulation in the thyroid. The acute exposure to Hg vapour results in ‘pink disease’ or acrodynia, bronchitis, asthma and temporary respiratory problems (Bernard et al. 2001). Hg(II) is one of the potent neurotoxins to humans due to its ability to cross the blood–brain barrier. It accumulates preferentially in the kidneys, is also absorbed in the gastrointestinal tract and reaches the bloodstream. During pregnancy, it enters the placental barrier and affects the nervous system of the developing foetus (Snyder 1971; Mizukoshi et al. 1975).

9.2.4 Cadmium

Cadmium (Cd) and its derivatives are highly virulent to humans. Cadmium is utilized in several industrial processes such as metal electroplating, Cd–Ni battery manufacturing, nuclear reactor control rods and shield preparation. Some derivatives are used as stabilizers for polyvinyl chloride. Cadmium (Cd) and zinc (Zn) have the same oxidation states, and hence, it can replace zinc’s position in metallothionein, thereby limiting it from working as a free radical scavenger inside the cell. When it binds to cysteine-rich proteins such as metallothionein, its concentration elevated 3000 times the normal and formed the cysteine–metallothionein complex. This causes hepatotoxicity in the liver, and then, it reaches the kidney, where it gets accumulated in the renal tissue and results in nephrotoxicity (Jaishankar et al. 2014).

9.2.5 Chromium

The occurrence of chromium (Cr) in the environment is due to the burning of fossil fuels from ferro chromate materials, pigment oxidants, catalysts, chromium steel, oil drilling processes, metal plating tanneries, etc. (Saha et al. 2011). Chromium is released into the aquatic environment through sewage and fertilizers. Cr (VI) is classified as a group 1 human carcinogen by the International Agency for Research on Cancer (Mancuso 1997). Chromium exists in two forms: trivalent and hexavalent. Due to its weak membrane permeability, trivalent chromium is harmless. Hexavalent chromium, on the other hand, is more active in penetrating the cell membrane through passages for isoelectric (SO_4^{2-}) and isostructural (HPO_4^{2-}) anion channels and ingested into the cell through phagocytosis (Su et al. 2005).

Heavy metal contamination and its ill effects alarmingly motivate the researchers to develop effective new technologies.

9.3 Phytoremediation Technology

The typical heavy metal remediation technologies such as containment (Mulligan et al. 2001a), solidification (Mulligan et al. 2001a), vitrification (Baker et al. 1994), mechanical separation technologies (Baker et al. 1994), pyrometallurgical separation (Diels et al. 2003), chemical treatments (Kurniawan et al. 2006), permeable treatment walls (Ludwig et al. 2002), electrokinetics (Pamukcu and Kenneth Wittle 1992), bioleaching (Sreekrishnan et al. 1993), biohydrometallurgical process (Veglio and Beolchini 1997), microbial remediation (Garbisu et al. 2002), biosorption (Yan and Viraraghavan 2001) and biomethylation (Kosolapov et al. 2004) were found to be costly, needed controlled environment, special reactor design, higher-energy consumption and usage of hazardous chemicals or large machineries (Mulligan et al. 2001a). The comparison of phytoremediation with aforementioned technologies was discussed in Table 9.2.

The advantages of phytoremediation over other technologies are:

- The plant itself acts as the bioreactor and eliminates the need for a reaction vessel and machinery.
- Plants are able to adapt to a wide range of climatic conditions, and the need for the controlled environment is optional (Brooker and Callaghan 1998).
- Phytoremediation is solar driven and therefore no external energy required (McIntyre 2003).
- The usage of chemicals was optional; genetically modified plants were used in the place of chemical amendments.
- There were no risk factors; after completion of the phytoremediation process, the plants were harvested; contaminants were recovered; and the remaining biomass can be utilized for the various purposes.
- This method was publicly accepted and practically possible.
- This method was reliable and cheap when compared to other existing technologies.
- Scale up of the process is possible and found to be very efficient for reclamation of contaminated lands in real time.

9.4 Phytoremediation Mechanisms

The aim of the phytoremediation was reclaiming contaminated lands using the plant–bioreactor, risk minimization, cost minimization required for the contaminated land treatment and environmental sustainability (Etim 2012). At the initial stage, the raw plants were utilized for the phytoremediation, and later, the recombinants with improved qualities required for the process were introduced. Plants are selected for the phytoremediation process based on the following criteria: survival–climate adaptation, plant's root morphology, soil type, the extraction ability or

Table 9.2 Comparison of physiochemical methods available for heavy metal remediation with phytoremediation technology

Remediation technology	Definition	Risk factors	Controlled environment conditions	Machineries	Chemicals	Energy
Containment	Physical barriers were used to contain the contaminated site and prevent both horizontal and vertical movement of contaminants	Contaminants remain active for years	Yes	Physical barriers made of steel, cement, bentonite, etc.	–	–
Solidification	Capping of contaminants by encapsulating inside a solid matrix reduces the contaminant movement chemically	Not suitable for heavy metals such as arsenic, mercury and chromium	Yes	Drum, large plants	Liquid monomers, cements	–
Vitrification	Solidification of contaminants using thermal energy by inserting electrodes into the contaminated soil	Produce toxic gases	Yes	Electrodes	–	Yes
Mechanical separation	Separation of contaminants from the contaminated site using mechanical methods such as hydrocyclone, gravimetric settling, centrifugation, etc.	Costly, energy consuming, high maintenance and operating cost	Yes	Hydrocyclone, high-powered magnets and centrifuge	Frothers or flocculating agents	Yes
Pyrometallurgical separation	Volatilization of metal from contaminated soil using high temperature	Energy consuming and require pretreatment of feed	Yes	High temperature furnace	Reducing or fluxing agents	Yes
Chemical treatments	Redox chemical treatment detoxifies or arrests the movement of contaminants	Exposure to chemicals	Yes	Chemical reactor	Oxidation or reduction agents	Yes

Permeable treatment walls	Permeable physical barrier contains reactive substance either physical, chemical or biological mode to detoxify or to reduce the mobilization of contamination at contaminated site itself	Low knowledge on optimization of flow and retention time through permeable barrier and media regeneration	Yes	Permeable physical barrier	Reactive substances for neutralization of contaminants	–
Electrokinetics	Contaminants were separated based on its charge by passing mild intensity electric current between electrodes planted to the contaminated soil	Large buried objects such as rocks and foundations interrupt the process	Yes	Electrodes	Buffers to maintain pH at electrodes	Yes
Bioleaching	Leaching of the metal from the contaminated soil using microbes	Contamination	Yes	Bioslurry reactor	Media, antifoaming agents	Yes
Biohydrometallurgical process	Hydrometallurgy’s subfield includes the microbes as potential tool	Contamination	Yes	Bioreactor	Media, antifoaming agents	Yes
Microbial remediation	The contaminants were remediated using microbes in the controlled environment	Contamination	Yes	Bioreactor	Media, antifoaming agents	Yes
Biosorption	Utilization of biologically derived materials for remediation of contaminants from the site of contaminants	More research needed to scale up the process	–	CSTR for batch process and column for continuous mode	Optional	Yes
Bio methylation	Methylation of metal contaminations using microbes	Contamination	Yes	Bioreactor	Media, antifoaming agents	Yes
Phytoremediation	Utilization of plant as bioreactor for remediation of contaminated site	–	–	–	Optional	–

degradation potential of the contaminants, growth rate, water transport, transpiration rate and high resistance to contaminants (Tangahu et al. 2011). The mechanisms involved in the phytoremediation of heavy metals are phytoaccumulation (inorganic contaminants), phytovolatilization (organic and inorganic contaminants) and phytostabilization (organic and inorganic contaminants).

9.4.1 Phytoaccumulation

In this methodology, plants uptake the metal contaminants and store them in the harvestable regions such as stem, roots and leaves as shown in Fig. 9.1. Heavy metal contaminants such zinc, copper, chromium, manganese, cadmium and lead are extracted by plants by their roots via this process (Hossner et al. 1998). The various terrestrial and aquatic plant species were explored to test their bioaccumulative capacity, and the plants with high accumulative capacity are called as hyperaccumulators. If a plant accumulates at least 1000 mg/kg (dry weight) of a specific metal or metalloid, they are classified as hyperaccumulators. Some notable hyperaccumulator plants used for the phytoremediation are *Pistia stratiotes*, *Spirodela polyrhiza*, *Myriophyllum aquaticum*, *Ludwigina palustris*, *Mentha aquatica*, *Nymphaea spontanea*, *Eichhornia crassipes*, *Centella asiatica*, *Cyperus rotundus*, *Brassica juncea*, *Zea mays* and *Ambrosia artemisiifolia* (Kamal et al. 2004). San Juan et al. (2018) reported the utilization of floating macrophytes such as *Limnobium laevigatum* and *Ludwigia peploides for remediation of lead- and zinc-contaminated water to evaluate its phytoaccumulation capacity. After the incubation period of 0–4 days in metal-containing solutions, the metal concentration on the* water, root and leaf samples was evaluated using atomic absorption spectroscopy. After 4 days of incubation time, both plants show a high metal removal efficiency of 70% from aqueous solution in all experimental cases. The high accumulation of zinc was noted in leaves,

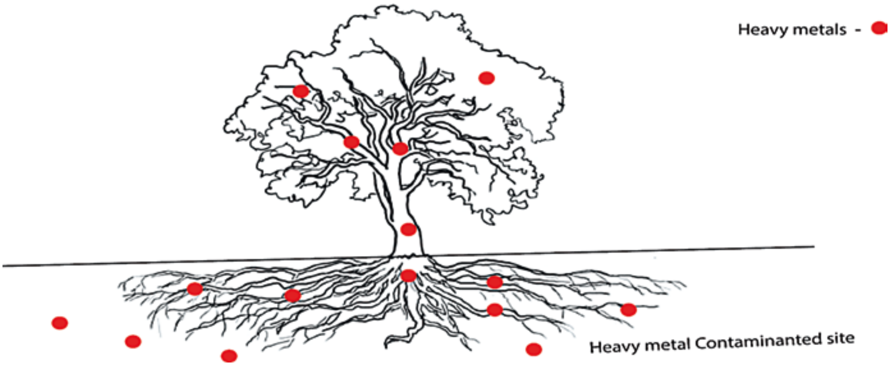

Fig. 9.1 Phytoaccumulation mechanism: plants absorb the contaminants and stored them in root, stem and leaves

and lead accumulation occurs in roots. Mosoarca et al. (2018) reported the phytoremediation of cobalt (1–15 mg/L) from wastewater using a submerged macrophyte *Elodea canadensis* and found that *Elodea canadensis* has hyperaccumulating potential for cobalt, the final cobalt concentration after the treatment was found to be less than 1 mg/L and the adsorption of cobalt ions to the *Elodea canadensis* follows Langmuir isotherm and the pseudo-second-order model equation. Ogundiran et al. 2018 discussed the compost and biochar-aided phytoaccumulation of lead using *Moringa oleifera* from the contaminated sites. Sunflower-poultry manure and rice husk (RHB)/groundnut shell (GSB) biochar were utilized as the compost and amendments. The addition of compost and amendments increases the biomass production, lead accumulation and lead phytostabilization potential in *Moringa oleifera*. The usage of compost, RHB and GSB with *Moringa oleifera* was recommended for the improved phytoremediation of lead. *Trees such as Eucalyptus tereticornis*, *Leucaena leucocephala*, *Melia azedarach* L and *Dalbergia sissoo* can be utilized for multipurpose, and so these trees were commercially important for utilization to remediate metal-contaminated land which resulted in solid-contaminated wood. The contaminated could be used for manufacturing of solid/composite wood products. Aforementioned plants were evaluated by Paisio et al. (2018) for their cadmium phytoextraction potential and found that *Melia azedarach* L shows more tolerance to Cd and *Leucaena leucocephala* had the high potential for phytoextraction of cadmium from the contaminated soil. The simultaneous removal of cadmium and phenol from the mixed contaminated site using *Lemna minuta* was possible. The plant shows high resistance towards mixed contaminants, and there are no notable changes in chlorophyll, carotene and malondialdehyde content which explains its antioxidant potential. This plant utilizes the phenol for growth and accumulates cadmium at a higher rate. So *Lemna minuta* can be used for the treatment of effluents containing phenol and cadmium as mixed contaminants. Bian et al. (2018) elaborate that the planting pattern affects the metal distribution and intercropping system increases the biomass yield. The intercropping of plants *P. praecox* and *S. plumbizincicola* improved the phytoremediation efficiency for removal of heavy metals from contaminated site.

9.4.2 Phytostabilization

In this method, the heavy metals were immobilized at contaminated sites itself and prevent the spreading of the contaminants to nearby lands as shown in Fig. 9.2.

The processes involved in the phytostabilization are:

1. Metals adsorbed onto root and root hair surface.
2. Stabilization of contaminants in the root zone: The plant produces enzymes and proteins within the root zone and precipitates or immobilizes the contaminants at the root zone itself.

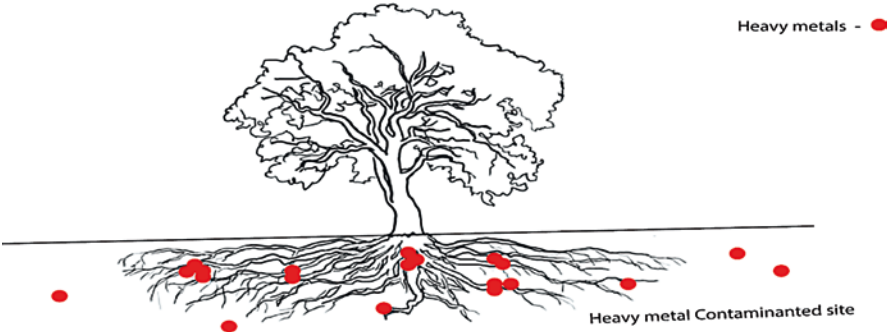

Fig. 9.2 Phytostabilization mechanism: plants stabilize the contaminants in the root zone itself and prevent them from entering into the food chain

3. The stabilization of contaminants in root membrane: The root membrane contains enzymes and proteins which can bind with the contaminants and stabilize the contaminants on the exterior portion of the root membrane.
4. Stabilization of contaminants inside the root cells: Once contaminants entered into the root membrane, few enzymes facilitate the transport of contaminants across the cell membrane and arrest it within the root vacuoles and prevent it from reaching the shoot system.

The plants with phytostabilization ability are *Agrostis* spp., *Festuca* spp., *Deschampsia cespitosa*, *Piptatherum miliaceum*, *Zygophyllum fabago*, *Lygeum spartum*, *Bromus inermis*, *Phleum pratense*, *Festuca pratensis*, *Alopecurus pratensis*, *P. tremula*, *Picea abies*, etc. (García et al. 2003). The polymetallic contaminants from the acidic mining site were remediated using *Medicago sativa* L with the application of powder marble as an enhancing agent which resulted in neutralization of acid mine tailings and increased the phytostabilization capacity of heavy metals (Midhat et al. 2018). The experiment was performed in greenhouse, and growth of the plant decreases with increase in powdered marble concentration; however, it increased the phytostabilization capacity of *Medicago sativa* L species. So this method was the good solution for neutralization and remediation of heavy metals from acid mine tailing (Midhat et al. 2018).

The phytostabilization of cadmium from the soil using five ornamental plants *Osmanthus fragrans*, *Ligustrum vicaryi* L, *Cinnamomum camphora*, *Loropetalum chinense* var. *Rubrum* and *Euonymus japonicus* Aureo-mar (*EJ*) was studied in greenhouse experimental conditions by Zeng et al. (2018). All five plants showed a normal growth, and soil microbial communities influence the process when the cadmium concentration present in the soil was less than 24.6 mg·kg$^{-1.}$ The amount of cadmium concentrated in leaves and stem was similar to all aforementioned ornamental plants after phytoremediation. The usage of these ornamental plants increases metal-contaminated soil enzyme activity. There was a notable increase in soil urease and sucrase activities; at the same time, dehydrogenase activity decreased. Sricoth et al. (2018) *carried out* hydroponic experiments on aquatic plants such as *Thalia* *geniculate*, *Cyperus alternifolius*, *Canna indica*, *Eichhornia crassipes* and *Pistia stratiotes* with a grass variety *Vetiveria zizanioides*. This study revealed that only *E. crassipes* and *P. stratiotes* possessed bioconcentration and translocation factors and are found to be suitable for the phytostabilization of cadmium and zinc. The aquatic plants such as *C. alternifolius* and *T. geniculate* were found to adapt well to the metal-contaminated site and stored a large amount of heavy metals in their roots. Brunetti et al. (2018) conducted the greenhouse experiment on 400 ha of contaminated land of *Apulia region* belonging to the national park using *Helichrysum italicum* (Roth) Don. The experiment was conducted in two cases with and without inoculation of *Septoglomus viscosum* to the contaminated site. From bioconcentration and translocation marker study, the process of heavy metal remediation from the soil was decrypted as phytostabilization process. *Helichrysum italicum* (Roth) Don shows increased biomass and growth in contaminated soil than the control soil in both experimental cases. Inoculation of *Septoglomus viscosum* to the contaminated site affected the heavy metal stabilization capacity of *Helichrysum italicum (Roth) Don*, which is a contrast to previously reported microbe–plant interaction and its positive effect on phytostabilization cases.

9.4.3 Phytovolatilization

In phytovolatilization, the contaminants from the soil were absorbed by the plants and released into the atmosphere after biotransformation into less toxic forms; this method was not considered as complete remediation solution because there is a chance for redeposition of the released products (less toxic forms) in nearby lands (Ali et al. 2013). The metals such as selenium and mercury were absorbed by the plants from the soil and converted into volatile forms such as dimethyl selenide and mercuric oxide and released into the atmosphere, the volatile compounds (dimethyl selenide, mercuric oxide) were less toxic than metallic form, but they still affect human beings.

The steps involved in the phytovolatilization process are:

1. Translocation of adsorbed contaminants (organic or inorganic) through the root modifies them to less toxic form within plant tissues.
2. The modified compounds were translocated to the leaves.
3. In leaves, they released into the atmosphere either using the process of transpiration (volatile gaseous form) or evaporation (released through the stomata in liquid form and gets evaporated) as shown in Fig. 9.3.

The plants such as *Canna glauca* L, *Colocasia esculenta*, *Cyperus papyrus* L, *Azolla caroliniana*, *Arundo donax* L, *Pteris vittata*, *Brassica juncea*, *Lupinus* sp., *Liriodendron tulipifera* and *Typha angustifolia* L were well known for the phytovolatilization of heavy metals (Pilon-Smits et al. 1999). The phytovolatilization of heavy metals was not suitable for the cities with high population density and places

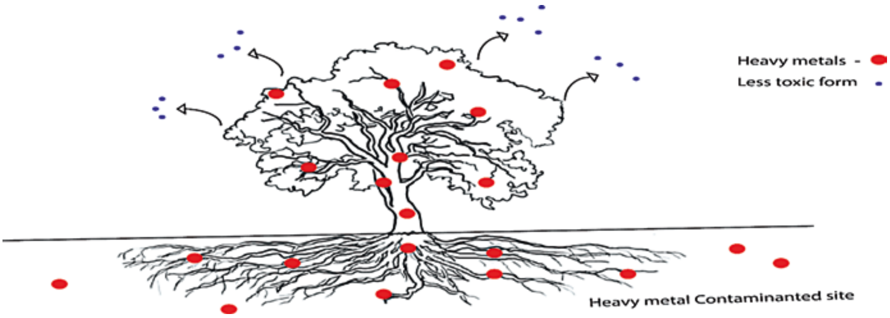

Fig. 9.3 Phytovolatilization mechanism: plants absorb and convert the toxic contaminants into less toxic form

with unpredictable weather patterns because it increases the chances for resettlement of volatilized contaminants.

The genetically modified *plants* expressing merb, mercuric reductase and bacterial organomercurial lyase are capable of absorbing divalent and methylmercury from the contaminated sites and release Hg (0) into the atmosphere (Rahman et al. 2008). The plant species such as *Chara canescens* and *Brassica juncea* had a high potential for phytovolatilization of selenium from the contaminated sites (De Souza et al. 2002). The plants used for remediation of selenium from water can be used as the supplementary cattle feed. *Nicotiana tabacum* var infected with *Agrobacterium* containing Ti plasmid with mera/merb dicistronic construct showed great resistance towards both phenylmercuric acetate and $HgCl_2$ (Rahman et al. 2008). The root lengths and dry weight of the recombinants were higher than the control plants. The plant species such as *Arabidopsis thaliana*, *Liriodendron tulipifera*, *Arachis hypogaea*, *Populus deltoides*, *Oryza sativa*, *Spartina alterniflora* and *Chlorophyta* were engineered with mera gene and proved to show high resistance to mercury chloride (0.04–100 mm) (Pant and Singh 2014). MerC-engineered *Arabidopsis thaliana* and *Nicotiana tabacum* showed increased accumulation of divalent Hg comparatively than the wild type.

9.5 Challenges in Phytoremediation

Although phytoremediation has a high potential for the treatment of metal-contaminated sites, they have few notable limitations:

- The phytoremediation of contaminated sites results in nonedible plant biomass (Kumar et al. 2008).
- Proper care and maintenance are required for phytoremediation site (Pivetz 2001).
- The plants may be prone to insect, pest or weed invasion, which results in reduced biomass (Mack et al. 2000).

- Volatilization of contaminants into the atmosphere in phytovolatilization pollutes the air and creates airborne problems (Heaton et al. 1998).
- Proper treatment of biomass is required before disposal (Rawat et al. 2011).
- The process is time-consuming and takes a long duration to clean up the contaminated site (Tangahu et al. 2011).
- Root contact is a major problem in case of herbs and shrubs; trees have long roots of 10–15 ft but take a long time to grow (Weber 2017).
- By-products formed from the contaminants during the phytoremediation process may remain toxic (Mulligan et al. 2001b).

9.6 Enhancements of Phytoremediation Process

The phytoremediation process can be enhanced by physiochemical processes such as chelators (EDTA, EGTA, etc.), biological process (genetically modified plants, plant–microbe interactions) and various agricultural practices like the construction of wetlands and growing energy crops in contaminated fields.

9.6.1 Chemical Mediated Enhancement

There are certain chemicals or surfactants which increase the mobility of metals in soil by lowering the surface tension between two liquids, between a gas and a liquid or between a liquid and a solid. Bagga and Peterson (2001) conducted a study where the application of 5 mmol kg^{-1} of *CDTA* to arsenic-contaminated test fields enhanced the accumulation of arsenic by their test plants. The plants accumulated up to 1400 ppm of arsenic as compared to 950 mm of arsenic accumulated by the plants without any chelating agents. In a study conducted by Wang et al. (2007), it was shown that application of chelating agent EDTA promoted the translocation of Pb into the overground parts of the plant, and chelation mechanism was shown in Fig. 9.4. The concentration was increased from 24.23–680.56 mg/kg to 29.07–1905.57 mg/kg in the overground parts of the plants. However, the application of the EDTA to the remediated lands also has potential environmental risks (Wu et al. 2004). Higher concentration of EDTA was lethal to plants (Hovsepyan and Greipsson 2007). Organic chelators such as citric acid helped to ameliorate the phytoextraction by increasing metal solubility in the soil. Application of 2.5 mM citric acid to contaminated fields increased the uptake of the cadmium by *Brassica napus L.* from 14.31 ± 0.4 μg to 23 ± 1.2 μg in the shoot and 3.60 ± 0.13 μg to 6.64 ± 0.60 μg in the root (Ehsan et al. 2014). It was found that EDDS is more effective than EDTA at increasing the concentration of Cu accumulation in corn and beans. In a pot experiment, the amendment of 5 mmol kg^{-1} EDDS to soil resulted in increased concentration of Cu in the shoot, with maximum levels of 2060 and 5130 mg kg^{-1} DW in corn and beans, respectively (Luo et al. 2005). It has been widely reported

Fig. 9.4 EDTA-mediated enhancement of heavy metal absorption: the chelate effect enhances the absorption of heavy metals by plants

that EDDS is a biodegradable chelate and has a strong affinity towards transition metals and radionuclides (Jones and Williams 2001; Grčman et al. 2003). NTA acts as synthetic chelating agents as it combines the property of high degradability with high chelating strength (Tiedje and Mason 1974; Bolton et al. 1996; Kulli et al. 1999). In a field study, Wenger et al. (2002) investigated the influence of NTA on the uptake of Zn, Cd and Cu by the test plants. It was inferred that NTA increased the solubility of Zn, Cd and Cu ions by a factor as much as 21, 58 and 9, respectively. The addition of these soil amendments to the field, apart from enhancing the phytoremediation process, also poses some environmental threats such as leaching of metals into the groundwater (Mulligan et al. 2001a; Wong 2003).

9.6.2 Genetically Modified Plants

Since the birth of recombinant technology, genetic engineering has been widely incorporated into practice to overcome the limitations of conventional biological techniques. Phytoremediation process can be enhanced by altering the genome structure of the hyperaccumulator plants. In doing so, the biomass production and metal uptake from soil can be significantly increased (Heaton et al. 1998; Gisbert et al. 2003; Eapen and D'Souza 2005). Metallothionein, metal transporters and alteration in oxidative stress mechanisms are some of the possible areas of genetic manipulation in the genome structure of plants. Metallothionein genes have the capacity to bind to both the physiological and xenobiotic heavy metals through its thiol group present in its cysteine residues (Eapen and D'Souza 2005). A cloned human MT-2 gene is transformed into *Brassica napus* and *Nicotiana tabacum* which grew in cadmium-contaminated field soil. The transgenic plants showed enhanced tolerance towards Cd, and the roots and shoots of the plants were remained unaffected by up to 100 μM $CdCl_2$ (Misra and Gedamu 1989). Similarly, Evans et al. (1992) performed a study where incorporation of the MT gene in *Arabidopsis thaliana* resulted in enhanced Cu accumulation. Phytochelatins are plant-derived chelators and are oligomers of glutathione. They are produced by the enzyme phytochelatin synthase. These phytochelatins act as an alternative for chemical chelators and have an important role in heavy metal detoxification (Cobbett 2000). The enzymes γ-glutamylcysteine synthetase and glutathione synthetase were overexpressed into Indian mustard. The resultant transgenic Indian mustard produced high levels of glutathione and phytochelatins showed enhanced Cd tolerance and accumulation (Zhu 1999; Zhu et al. 1999). Genetic modification of metal transporters can result in altered metal tolerance and accumulation in plants. When a Zn transporter—ZAT gene—from *Thlaspi goesingense* is introduced into *Arabidopsis thaliana*, Zn accumulation in roots was twofold higher than the control plants (van der Zaal et al. 1999). Oxidative stress is an intricate physiochemical mechanism that incorporates all the biotic and abiotic stress in higher plants and occurs as a result of the accumulation of reactive oxygen species (Demidchik 2015). Alteration in the oxidative stress mechanism can recuperate the metal tolerance in plants (Eapen and D'Souza 2005). The Al tolerance in *Arabidopsis* plants can be enhanced by overexpressing the glutathione-*S*-transferase and peroxidase enzymes (Ezaki et al. 2000). However, the main limitation with the genetically modified organism is the ethical committee. There are certain safety and regulatory affairs which restrict the use of such plants for commercial purpose (Conner et al. 2003).

9.6.3 Plant–Microbe Assemblies

Rhizobacterium is a root-colonizing bacterium that forms a symbiotic relationship with a wide range of hyperaccumulator plants. This symbiotic relationship can be used to enhance the phytoremediation of heavy metals (Rajkumar et al. 2012). Certain metabolites such as indole-3-acetic acid and siderophores produced by plant–microbe interaction are known to alleviate metal detoxification in the rhizosphere of the soil (Glick 2010). The organic and inorganic compounds produced by the symbiotes have the chelating ability as that of the chemical chelators. Siderophores are iron chelators produced by most plant-associated microbe and fungi in response to low iron levels in the rhizosphere of the soil. Other than iron, it can also form stable complexes with most xenobiotics prevailing in the soil (Schalk et al. 2011). The rhizosphere bacterium *Pseudomonas aeruginosa* produces pyoverdine and pyochelin in association with maize which increase the uptake of bioavailable Cr and Pb in the soil (Braud et al. 2010). Likewise, in a study conducted by Dimkpa et al. (2009), *Streptomyces tendae* F4 produced siderophores which significantly enhanced the accumulation of Cd by sunflower plant. Another interesting compound produced by plant–microbe association is low molecular weight organic acids. They are known to have a property of heavy metal solubilization in the rhizosphere (Jones 1998). 5-Ketogluconic acid is a gluconic derivative produced by *Gluconacetobacter diazotrophicus* and aids in the solubilization of Zn and Zn-related complexes (Saravanan et al. 2007). The airborne bacteria isolated from the environments of tanneries in association with *Pseudomonas aeruginosa* produced 2-gluconic acid were able to accumulate ZnO from the rhizosphere (Fasim et al. 2002). Another important method to improve metal solubilization and phytoremediation process is to use microbially produced biosurfactants. These biosurfactants have the capability to form complexes with heavy metals found in the soil, thereby assisting in the process of metal accumulation by the plants (Juwarkar et al. 2007; Sheng et al. 2008; Venkatesh and Vedaraman 2012). *Pseudomonas aeruginosa* BS2 produces a biosurfactant known as di-rhamnolipid which aids in the accumulation of Cd and Pb by the test plants from the contaminated soil (Juwarkar et al. 2007).

9.6.4 Agricultural Work Practices

The growth of the plant and the symbiotic relationship with microbes can be improved by making use of certain agricultural work practices. This agricultural practice includes the addition of fertilizers, growing energy-yielding crops and providing enough carbon sources for the growth of the plant. Perennial crops such as *Populus*, *Ricinus*, *Jatropha* and *Miscanthus* grow rapidly and are very important for the biofuel production. By growing these energy-rich crops in the contaminated field sites further helps in energy production (Rockwood et al. 2004; Bauddh and Singh 2012). Wetland construction is another good agricultural work practices which alleviate the effect caused by heavy metal pollutants by trapping them by landscaping the field (Xiaoyong 2006).

9.7 Disposal of Contaminated Phytoremediation Biomass

Phytoremediation plays a major role in cleansing the heavy metal pollutants in the soil. However, the contaminants accumulated by the plant biomass, in turn, pose a threat to the environment by entering the food chain (Rai 2008). Hence, the phytoremediation process needs a proper disposal management method to prevent its flow into the food chain. The various techniques proposed for the post management of biomass are as follows.

9.7.1 Composting and Compaction

This process involves leaching of composting material to the plant biomass which forms soluble organic compounds thereby increasing metal solubility. Hetland et al. (2001) demonstrated that composting greatly reduced the volume of the contaminated plant biomass. Compaction is like composting where the leachate is collected from the site and treated accordingly with suitable soluble organic compounds.

9.7.2 Combustion and Gasification

In combustion, the plant biomass is burned under controlled conditions, and the volume is reduced to 2–5%, leading to the generation of electrical and thermal energy (Ghosh and Singh 2005). Likewise, in gasification, the plant biomass undergoes a series of chemical changes and results in the yield of clean and combustive gas which can be used as a fuel for economic purposes (Hetland et al. 2001).

9.7.3 Phytomining and Pyrolysis

Phytomining involves the natural uptake and preconcentration of bioavailable metal species from the contaminated fields into the plant tissues. It is a potential economic exploitation of the contaminated fields with minimal to no impact on the environment (Patra and Mohanty 2013). In pyrolysis, under anaerobic condition, the contaminated plant biomass is decomposed to produce pyrolytic fluid and coke. An advantage in phytomining is that the heavy metal residue remains in the coke, and this can be used as a substitute for the smelting process (Bridgwater et al. 1999).

9.8 Economic Opportunities of Phytoremediation Biomass

9.8.1 Biosorbent Preparation

Adsorption is another popular and widely practiced method for removal of metals (Sivarajasekar 2007; Sivarajasekar et al. 2017d, e), pharmaceuticals (Sivarajasekar et al. 2017a, b; Sivarajasekar et al. 2018a), dyes (Sivarajasekar et al. 2009; Sivarajasekar 2014; Karthik et al. 2018; Sivarajasekar and Baskar 2018b), fluoride (Sivarajasekar et al. 2017c, e), pesticides (Paramasivan et al. 2019) and other contaminants from the aqueous solution. Biosorption is the utilization of agricultural wastes such as immature cotton seeds, waste fruit shell and algae biomass for preparation of functionally active adsorbent. Biomass of plants utilized for phytoremediation such as *Salix rosthornii Seemen*, *Thalia dealbata*, *Vetiveria zizanioides* and *Phragmites* sp. is harvested from the contaminated site after utilizing for the remediation purpose and carried out pyrolysis at 500 °C in the nitrogen environment and under different temperatures (500, 600 and 700 °C) in a carbon dioxide environment to produce biochar. The cation-exchange capacity and specific surface area of prepared biochar vary with plant type as well as temperature. Biochar produced *by T. dealbata* at 600 °C was identified as the effective adsorbent for remediation of ammonium and phosphate from water (Zeng et al. 2013). Willow plant was used for a long time for the phytoremediation of heavy metals, after utilized for remediation purpose the biomass can be converted into biochar for the commercial application such as biosorbent and natural soil amendment through pyrolysis at high temperature 350–650 °C, under a steady flow of argon gas, set at either 100 or 500 ml min^{-1}. The obtained biochar has a high fixed carbon content and mesoporous structure at temperature 450 °C (Břendová et al. 2015). The biochar prepared from the waste biomass can be utilized as natural amendments, as the addition of biochar to metal-contaminated soil decreases the bioavailability and phytotoxicity of heavy metals during the phytoremediation process (Wiszniewska et al. 2016).

9.8.2 Bio-oil

The plants utilized for remediation purpose can be synergistically utilized for the bio-oil production. Utilization of such plants for remediation purpose increases the economic opportunity of generated waste biomass. The production of bio-oil from metal-containing waste biomass involves the following steps:

- Separation of metal residues present in the biomass using physicochemical techniques such as fast pyrolysis, enzymatic hydrolysis and acid hydrolysis
- Conversion of biomass into high-quality bio-oil of commercial value as shown in Fig. 9.5

The perennial plants such as *Miscanthus*, *Ricinus*, *Jatropha* and *Populus* were reported as suitable plants for phytoremediation of heavy metal, and these plants also help to meet our energy needs. The conversion of metal-containing fir biomass into bio-oil was reported by Liu et al. (2012). Here, bio-oil was generated as a by-product during the fast pyrolysis of fir biomass; the conversion is possible even the biomass contains metal contaminants. It was found that the copper present in the fir plant biomass catalysed the thermal decomposition of biomass and improve the bio-oil quality. Ruiz-Felix et al. (2016) studied the effect of various process routes, fast pyrolysis, enzymatic hydrolysis and acid hydrolysis, and their combinations for the conversion of switchgrass into sugars and biomass. The sugars produced from switchgrass through enzymatic hydrolysis and acid hydrolysis routes have no metal residues. But the chemical properties of bio-oil vary for each route, and biochar yield from the combined route utilizing all three methods was found to have a low concentration of lead (2 mg/kg). The biofuel meets huge market demand in the current global energy market due to its eco-friendly nature, efficiency and low cost. So, the conversion of phytoremediation plants into biofuel has huge demands and has been reported as the novel way for the disposal of the metal-contaminated plant biomass.

The biofuel production from the microalgae biomass utilized for the domestic wastewater treatment was done by lipid extraction and transesterification of lipid into biofuel. The microalgae lipids were extracted from the biomass through solvent extraction and quantitatively measured using Nile red fluorescence microscopy, Nile red spectrofluorometry, FTIR, TLC, HPLC and GC coupled with mass spectrometry (Rawat et al. 2011). During the transesterification process, the raw lipids

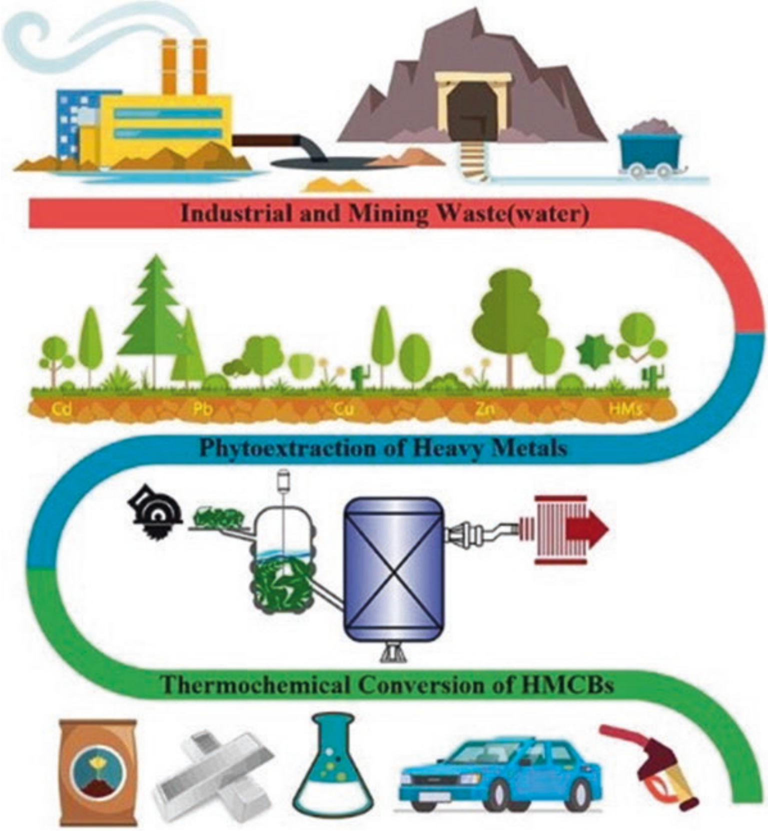

Fig. 9.5 Conversion of heavy metal-contaminated biomass (HMCB) obtained from the phytoremediation into biofuel using pyrolysis process (Reproduced from Dastyar et al. (2019). Copyright obtained from Elsevier)

were converted into biofuel, and addition of alcohol to the processing system maintains the biofuel conversion at positive scale towards product formation. Thermal conversion of microalgae biomass into biofuel is also possible with gasification, liquefaction, pyrolysis and combustion (Prasad 2015). The microbe-mediated fermentation of microalgae biomass yields bioethanol and biogas, and fermented biomass remains. The bioethanol and biogas were used to generate electricity, and fermented biomass remains can be utilized as biofertilizer. The thermochemical conversion of metal-containing phytoremediation biomass into commercial products was shown in Fig. 9.6.

The *Brassica napus* commonly known as rapeseed was identified as potential crop for remediation of metal-contaminated sites. After harvesting the plant from contaminated sites, the seeds are removed and processed to obtain bio-oil. The process involved in the extraction of bio-oil from biomass and conversion of extracted bio-oil into biodiesel was as follows:

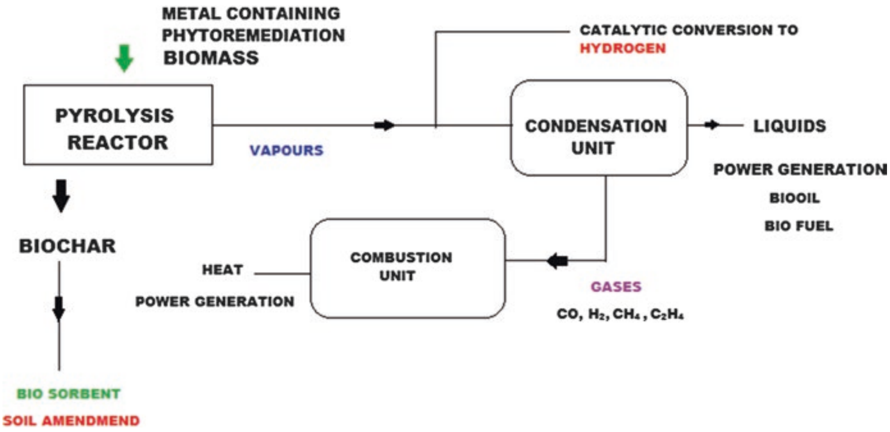

Fig. 9.6 Thermochemical conversion of metal-containing phytoremediation biomass into biofuels and biochar

1. Clean the seeds to remove impurities and dust.
2. Precondition the seeds by mild heating in a controlled environment.
3. Flake the preconditioned seeds.
4. Cook the flake.
5. Press the flake to separate oil and cake.
6. Liquid extract cake with hexane to remove remaining oil.
7. Refine the crude oil.

Conversion of extracted bio-oil to biodiesel

8. The refined bio-oil can be used together with diesel as fuel.
9. Pyrolysis of oil.
10. Microemulsification with alcohol.
11. Transesterification of bio-oil into biodiesel in the presence of excess alcohol.

9.8.3 Biogas

The presence of heavy metals in the anaerobic digestion system affects the biogas production and identified as concentration dependent. The silver nanoparticle concentration less than 40 mg/ml has less or no effect on anaerobic digestion and methanogenic population in batch anaerobic digester system. The aquatic plants such as water hyacinth (*Eichhornia crassipes*) and channel grass (*Vallisneria spiralis*) were utilized for phytoremediation of industrial effluents and subsequently utilized for biogas production. The biogas produced from the metal-containing plant biomass was greater than the plant that grows in deionized water. Channel grass produces biogas in the 6th day itself, but for water hyacinth, it's around 9 to 12 days (Singhal and Rai 2003). The presence of heavy metals such as copper, cobalt, zinc and lead in anaerobic digestion system affects the biohydrogen and methane production. Chromium, cadmium and nickel affect the bacterial population involving in the fermentation process by binding to the thiol group of vital enzymes, replacing the naturally occurred metal ions from the prosthetic group which results in inactivation and disruption of enzyme function (Mudhoo and Kumar 2013). The absorption of heavy metals by *Azolla pinnata* R. Br and *Lemna minor* L has a significant effect on the biogas production. The absorption of iron and manganese has no effect in biogas production, but copper, cobalt, zinc and lead have a negative effect, whereas cadmium and nickel increase the rate of biogas production. The methane content of biogas produced from Cd- and Ni-contaminated biomass was greater than the non-contaminated biomass (Jain et al. 1992).

9.8.4 Biofortification

About half of the world's population suffered from nutritional deficiency which can be eliminated by fortification of food crops with essential minerals. In olden days, the food crops were fortified with the application of metal-enriched fertilizer, soil amendments and chelators (Reilly 2008). The biofortification of food crops with micronutrients such as selenium, iron and zinc plays an important role in combating the nutritional deficiencies across the global population. Usually, fortification of food crops was achieved through applying fertilizers or biotechnological means such as crop breeding or recombinants, but these methods are costly and involve lots of technical difficulties. Nowadays, researchers proposed a solution for biofortification of food crops in a cost-effective manner through phytoremediation coupled with biofortification strategy (Thangavel and Subbhuraam 2004).

The hyperaccumulator food crops were utilized for remediation of aforementioned metal-contaminated sites and subsequently processed into biofortified food and agricultural products in the controlled environment. Carrot and broccoli grown in soil amended with selenium hyperaccumulator biomass result in biofortification; the increase in selenium concentration was observed in edible parts of the aforementioned vegetables (Bañuelos et al. 2015). The concentration of selenium was maintained within the permissible range by adjusting the quantity of selenium-enriched soil amendment. The biofortification process utilizes plants secreting metal complexing compounds which limit the bioavailability of heavy metals for controlled biofortification. Methods such as intercropping of two hyperaccumulators; modifying the soil nature, i.e. pH; and applying metal-enriched fertilizers and synthetic metal chelators can improve biofortification process. Plants such as *Triticum aestivum*, *Brassica* sp., *Agaricus bisporus*, *Lentinus edodus*, *Grifola frondosa*, *Pleurotus eryngii* and *H. tessulatus* were studied for the biofortification ability of selenium and reported by Banuelos et al. (2013).

9.8.5 Nanoparticle Synthesis

The plants absorb the metals from soil or growth media and reduce it to the nanoparticles through their metabolic pathways and stored them in stem, leaf and roots (Shekhawat and Arya 2009; Marchiol 2012).

The examination of sectioned plant parts with UV–visible spectroscopy, EDX, TEM, atomic absorption spectroscopy, XRD and X-ray absorption spectroscopy confirmed the formation of metal nanoparticles within the plant tissues. Beattie and Haverkamp (2011) reported that the *Brassica juncea* 2-week-old seedlings absorbed and reduced the silver nitrate into silver nanoparticles. The chloroplast plays important role in the reduction of absorbed metal into nanoparticles due to the presence of high level of reducing sugars (glucose and fructose) within the plant tissue The aqueous plant extracts of *Triticum aestivum*, *Avena sativa*, *Medicago sativa*, *Cicer arietinum*, *Pelargonium graveolens*, *Aloe vera*, *Cymbopogon flexuosus*, *Cinnamomum camphora*, *Azadirachta indica*, *Tamarindus indica*, *Emblica officinalis* and *Leucas aspera* were utilized for the reduction of silver nitrate into silver nanoparticles at constant stirring (Masarovičová and Kráľová 2012). The aqueous plant extracts contain primary and secondary metabolites such as antioxidants, flavonoids, flavones, isoflavones, catechins, anthocyanidins, isothiocyanates, carotenoids and polyphenols which are responsible for the reduction of metal source liquid into nanoparticles. The art of nanoparticle formation within the plant tissue and its mechanism are still not clear (Masarovičová and Kráľová 2012).

9.8.6 Solid/Composite Wood Products

The perennial plants used for phytoremediation were removed from the treated site and converted into solid/composite wood products. The tolerance of birch tree against the metal was directly related to the physicochemical property of the soil where it germinated; the birch clone collected from the metal-contaminated site showed a great resistance against similar metal but low resistance for other metals (Kopponen et al. 2001). So phytoremediation of heavy metals using birch tree should be designed as in situ operation. The phytoremediation of heavy metals with trees has great advantage over the small plants. The trees have increased metal accumulation potential and tolerance than small plants, and biomass production was more, which resulted in high accumulation of metal per kg biomass per square area (Ledin 1996). Jobling and Stevens (1980) reported that the trees are not suitable for remediation of mine spoil heaps due to its physical and hydrological properties.

The steps involved in conversion of wood logs to timber were as follows:

1. Mature tree from treated site was identified and harvested.
2. The harvested logs are stored in the site temporarily to evaporate the free water content and to cut the small side branches.

3. The harvested logs are transported to the saw mill using trucks equipped with lift gears.
4. In saw mill, the logs were processed into the wooden boards using round and band saw machines and that the process involved rough cutting of logs (breaking) and resawing to improve the precision and accuracy of cutting.

9.9 Conclusion

The plant-based treatment methodologies are the current research trends due to their eco-friendly nature. The effects of heavy metal on the animal, aquatic and animal biota are significant, and it should be given primary attention. Heavy metal removal from contaminated sites using different phytoremediation methods has been discussed in this review elaborately. It seems that the plants were selected and phytoremediation was carried out based on the metal toxicity and plant efficiency. Many of the authors have established the efficient phytoremediation methods for almost all the heavy metals. However, the challenges they have encountered are also addressed in this review. The heavy metal-contaminated plants after treatment are the big question before every researcher. This review has consolidative addressed the efficient and economically viable post-harvesting technologies to dispose the contaminated plants. From this review, recent literatures indicate that there are a lot of avenues for research in the post-harvesting technologies and efficiency improving methods for phytoremediation.

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Chapter 10
Adsorptive Removal of Toxic Dyes Using Chitosan and Its Composites

Swati Verma and Raj Kumar Dutta

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Abstract Adsorption is considered to be one of the most efficient and cost-effective processes for the removal of pollutants including dyes from polluted water bodies. Wide range of materials is being studied for removing dye molecules that impart colour to water. Chitosan has emerged as a low-cost, non-toxic, biodegradable and easily available option for removing dye molecules by adsorption. The functional

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S. Verma
Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee, India

R. K. Dutta (✉)
Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee, India

Centre of Nanotechnology, Indian Institute of Technology Roorkee, Roorkee, India
e-mail: duttafcy@iitr.ac.in

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groups in chitosan, e.g. the hydroxyl and the amino groups, are responsible for the adsorption of cationic as well as anionic dyes. Here we have discussed some of the significant cases of cationic and anionic dye adsorption by chitosan. Broadly, chitosan-based adsorbent can be categorized as (a) grafted and cross-linked chitosan to enhance adsorption capacity and also to impart superior mechanical stability so that the adsorbent can be used in harsh condition and (b) composites with wide range of materials, e.g. clay, carbon materials, other polymers and metal oxides. Further sizes and morphologies, e.g. sphere, beads, nanofibres, have effects on the adsorption capacities. In addition, the scope for adsorptive photocatalytic dye degradation has been discussed. For this purpose, ZnO–chitosan nanocomposite is taken as a model adsorbent cum photocatalyst for removing Congo red anionic dye, where chitosan facilitated adsorption while ZnO favoured dye degradation.

Keywords Chitosan · Composites · Dye · Adsorption

10.1 Introduction

Increased industrialization, urbanization and agricultural activities elevated the concentrations of toxic chemical compounds in water (Jayaswal et al. 2018). Consumption of polluted water is linked with health hazards and can have fatal consequences (Schwarzenbach et al. 2010). These toxic compounds include pesticides, phthalates, polyaromatic hydrocarbon, phenols and its derivatives, industrial dyes and heavy metals (Shahat et al. 2015; Chequer et al. 2013; Dutta et al. 2019). Among these, dye industries are one of the most significant point sources for water pollution. They are toxic in nature and are carcinogenic to human beings and aquatic lives (Sharma et al. 2015; Daneshvar et al. 2017). Dyes are organic compounds that impart colour to water, and therefore, they are widely used for colouring applications in textile, paints, leather, cosmetics, plastic, paper and photographic industries (Christie 2001). Industries are using large amounts of water for dyeing applications, and the unregulated discharge of dye effluent into mainstream water bodies without any treatment process is dangerous for the environment. Also, most of the dyes can persist in the environment for long periods as they are resistant to natural degradation processes such as thermal, biological and photodegradation. These dyes when present in water hinder the photosynthesis process and therefore affect the ecosystem of aquatic plants and animals. In humans, azo dyes can be metabolized into aromatic amines and N-hydroxylamines which cause severe damage to DNA (Rajaguru et al. 1999, Pinheiro et al. 2004, De Aragão Umbuzeiro et al. 2005). Therefore, removal of toxic dyes from wastewater is necessary to avoid any potential hazard to the environment and its creatures.

Adsorption is one of the most widely used decontamination techniques for the removal of dissolved impurities from one phase to another (Naushad et al. 2016). It is a mass transfer phenomenon which involves accumulation of dissolved material

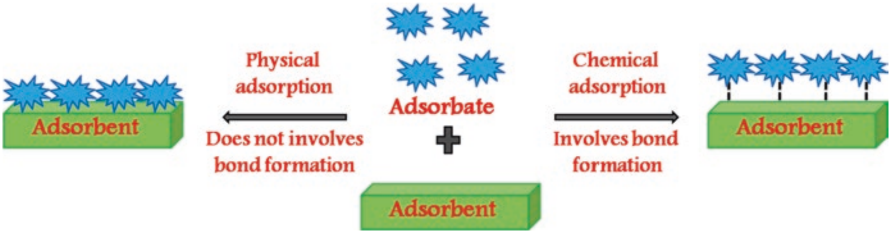


Fig. 10.1 Physical and chemical natures of adsorption process

called *adsorbate* on the surface of a solid material called *adsorbent*. It is governed by various physical (does not involve formation of new bonds) and chemical (involves formation of new bonds) forces and depending upon that adsorption can be reversible or irreversible (Fig. 10.1). Several other factors such as pH, temperature, concentration and contact time also affect adsorption phenomenon. Many adsorbents have been developed with an ability to remove toxic organic dyes from aqueous solution via adsorption process. Based on the resources, adsorbents can be classified as either natural or synthetic. Wide range of adsorbents are being explored which include bio-adsorbents like algae and fungi; readily available in nature, e.g. clay, mud and coal; synthetic materials, e.g. activated carbon, graphene and carbon nanotubes; and inorganic adsorbent like silica, alumina, zeolites, zinc oxide, iron oxides, etc. (Rafatullah et al. 2010, Dabrowski 2001). In addition, there have been significant studies on exploring industrial, municipal and agricultural wastes as adsorbent (Gupta 2009). The important features for a material to qualify as a good adsorbent are high adsorption capacities with high selectivity, reusability and low cost. In view of this, polymeric materials, particularly polysaccharides/biopolymers such as starch, chitin, chitosan and cellulose, have gained interest as alternative adsorbents or functionalizing the surface of adsorbents for the removal of dyes (Crini 2005). These are also low-cost natural adsorbent which does not pose any threat to the environment after their usage. These materials contain oxygen and/or nitrogen bearing functional groups which favour adsorption of dyes. The structural and physico-chemical characteristics of these materials provide opportunity of surface modifications which helps in achieving enhanced adsorption properties. Chitosan is one of the most widely studied adsorbents including other polysaccharides like cellulose and starch, due to high abundance and low cost (Crini 2006). Here we will discuss different cases of chitosan and their composites as an adsorbent.

10.2 Physico-chemical Properties of Chitosan

Adsorption involves interaction between adsorbate and adsorbent. Therefore molecular structure of the adsorbent would be decisive to explain the adsorption properties of the adsorbent. Chitosan is an acetylated derivative of chitin, which is a

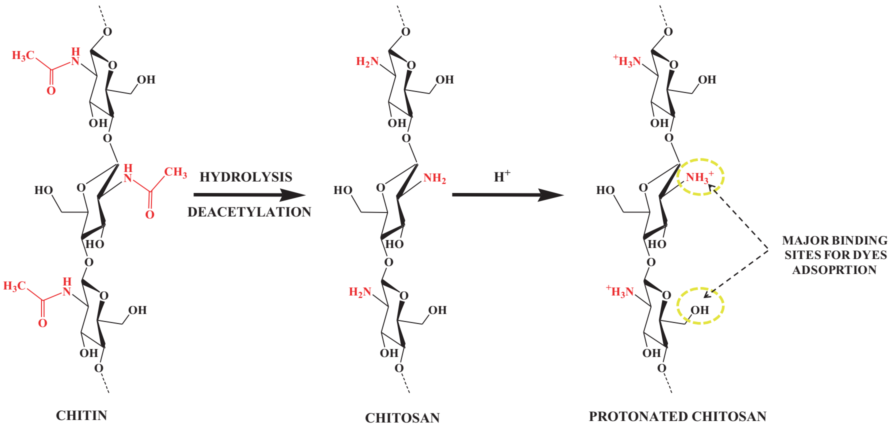


Fig. 10.2 Chemical structures of chitin, chitosan and protonated chitosan

naturally occurring amino polysaccharide, and it is also known as poly-β-(1→4)-*N*-acetyl-D-glucosamine. The chemical structure of chitin is given in Fig. 10.2. It is obtained by the alkali treatment of the exoskeleton of crustaceans and shrimp, cartilages of molluscs, cuticles of insects and cell walls of microorganisms (Abdou et al. 2008). Chitosan is a common name of poly-β-(1→4)-2-amino-2-deoxy-D-glucose, which is deacetylated derivative of chitin. It is derived by the alkaline hydrolysis of chitin, which causes conversion of *N*-acetyl ($-NHCOCH_3$) groups into amine ($-NH_2$) groups. The degree of deacetylation of chitosan is the ratio of the total number of deacetylated units to the number of acetylated units. It is also a measure of number of $-NH_2$ groups which offer sites for binding with adsorbate molecules or ions. It may be remarked here that chitosan has found wide applications in different domains of science and technology, including an important adsorbent due to its low cost and non-toxicity. It should be stressed here that the toxicity of the adsorbent is an important specification as the spent adsorbents are often disposed in landfill.

One of the most important applications of chitosan is in the removal of pollutants such as organic dyes or toxic metal ions from contaminated water (No and Meyers 2000). The presence of hydroxyl and amine functional groups in chitosan plays vital role in the adsorption of pollutants from aqueous solution (Albadarin et al. 2017; Sharma et al. 2017). The most promising characteristic of chitosan is its chemical structure that allows chemical and physical modifications to enhance its adsorption ability. Chitosan with lower degree of deacetylation exhibits superior adsorption capacity towards acidic dyes as compared to chitosan with higher degree of deacetylation (Wong et al. 2008). This is due to the modifications in the internal structure of chitosan during deacetylation process which causes reduction in adsorption capacity. Other factors like crystallinity, weight and distribution of acetyl and amine functional groups also affect adsorption characteristics of chitosan (Jaworska et al. 2003; Guibal and Roussy 2007). For example, high molecular weight chitosan exhibits poor solubility at basic pH because of intermolecular hydrogen bonding. But at acidic pH, chitosan shows excellent solubility due to the protonation of its amine groups. Similarly, poorly crystalline chitosan displays low adsorbent capacity due to the inaccessibility of amine and hydroxyl groups. Chitosan being a potential adsorbent suffers from many drawbacks, such as its poor thermal and mechanical strength (Guibal 2004), poor stability in acids (Zhou et al. 2009), low porosity and poor surface area (Alhwaige et al. 2013; Crini and Badot 2008). However, unlike several other polysaccharides, chitosan can be transformed into different morphologies like beads (Lee et al. 2014), nanofibres (Schiffman and Schauer 2007), membranes or films (Salehi et al. 2016) and nanoparticles (Shajahan et al. 2017) to increase its chemical functionality and mechanical and acid stability. Mechanical stability and adsorption capacity of chitosan have also been increased by making composites with clay, bentonite, montmorillonite, activated carbon, graphene oxide and metal oxide nanoparticles (Ngah et al. 2011; Zhang et al. 2016a, b; Chen et al. 2013; Reddy and Lee 2013). In subsequent section, we will discuss some selected cases where chitosan was used as adsorbent for dye removal.

10.3 Raw Chitosan

Several studies are being reported on the adsorption of dye molecules by pure chitosan. Mostly the researchers attributed the amine and hydroxyl groups in chitosan as binding sites for adsorption of dye molecules. It is important to mention that dye compounds can be broadly categorized as acidic dye, basic dye and reactive dye. The nature of interactions between dye molecules and chitosan depends upon the functional groups in dye. Acidic dyes are water-soluble anionic dyes which contain one or more sulfonic acid groups or other acidic groups. Therefore, adsorption of acidic dyes by chitosan occurs at low pH values where the negatively charged functional groups of dyes can bind electrostatically with the protonated binding sites of chitosan, mainly with NH_3^+. On the other hand, basic dyes are cationic water-soluble dyes which contain one or more electropositive centre and therefore exhibit lower adsorption values as compared to acidic dyes with chitosan-based adsorbents. Apart from acidic and basic dyes, chitosan-based adsorbent has been widely studied for the removal of reactive dyes from aqueous solution because these dyes contain a reactive that can form chemical bond with the hydroxyl and amine functional groups of the chitosan. The adsorption of reactive dyes by chitosan is a fast process and often displays very high adsorption capacity values.

In 2015, Pietrelli et al. reported the adsorptive removal of different types of dyes such as Telon B red (acidic dye), astrazon GTLN red (basic dye), Remazol RR gran yellow (reactive dye) and Scarlet red 23 (direct dye) by pure chitosan (Pietrelli et al. 2015). They performed adsorption experiments in batch mode as a function of pH, temperature, contact time, initial dye concentration and grain size. Under similar experimental conditions, the order of dye adsorption by chitosan was acidic > direct > reactive > basic dyes. As compared to basic pH, the adsorption of dye by chitosan was more at acidic or neutral pH. This is due to protonation of amine group at lower pH which is responsible for electrostatic interactions between chitosan and dye molecules. This led to exploring adsorptive removal of different types of dye molecules by modifying chitosan at suitable pH. The ability of chitosan to get protonated at low pH is therefore expected to favour removal of anionic or acidic dye from wastewater.

Wong et al. conducted studies on the removal of various kinds of acid dyes such as acid green 25, acid orange 10, acid orange 12, acid red 18 and acid red 73 from aqueous system (Wong et al. 2003). For an optimized dose of chitosan as adsorbent and pH of the dye solution, the maximum adsorption capacities were 645.1, 922.9, 973.3, 693.2 and 728.2 mg/g, respectively. These values were determined from Langmuir adsorption isotherm, which implied that the dye interaction with chitosan is largely due to adsorption at the surface of the chitosan. The difference in the adsorption capacities was attributed to the molecular sizes and number of sulfonic acid groups attached to dye molecule. The optimum contact time was 24 h and the dye adsorption followed Langmuir isotherm model. Several other researchers also studied adsorption of anionic dye using chitosan as adsorbent (Pathania et al. 2016; Dos Anjos et al. 2002; Saha et al. 2010; Maghami and Roberts 1988; Kumar 2000). Thermodynamic results further showed that the process of dye uptake by chitosan is a spontaneous and an endothermic process. Though adsorption is primarily an exothermic process, these studies revealed that the adsorption capacity is enhanced at higher working temperature. Such anomalous behaviour is attributable to the need of activation energy for dye adsorption.

In addition, researchers also found it interesting to study adsorption of basic or cationic dyes by chitosan. However, the maximum adsorption capacity achieved in the case of basic dyes is lower as compared to acidic dyes. This is attributable to unfavourable electrostatic interactions between the positively charged chitosan and positively charged dye molecules (Annadurai 2002). In that case the observed order of cationic dye adsorption on chitosan is attributable to other forms of interactions, especially via π–π interaction between the six-membered rings of dye molecules and those in the molecular structure of chitosan. Adsorption of basic dye and reactive dyes occurs at higher pH due to the interaction of free electron pair of nitrogen with the electropositive centre of dye molecules. They have further showed that adsorption of different dyes on chitosan follows Langmuir adsorption isotherm indicating monolayer nature of adsorption.

The adsorption capacity of chitosan is also found to be influenced by the degree of deacetylation (Jóźwiak et al. 2017). Chitosan flakes with three different degrees of deacetylation, i.e. 75, 85 and 90%, were tested for the adsorption of a textile dye reactive black 5 from aqueous solution. It was found that chitosan flake with 90% degree of deacetylation reveals highest adsorption capacity of 1049.6 mg/g. This value is 160 times than more than that of chitosan with 75% degree of deacetylation. Deacetylation of chitosan results into incorporation of more number of amine groups. Therefore the drastic increase in the adsorption capacity of chitosan due to increased deacetylation is attributable to availability of higher number of amine sites on chitosan. Other studies also support the concept of achieving high adsorption efficiency with chitosan flakes having high degree of deacetylation and vice versa (Kim et al. 1997). Thus, it can be concluded that unmodified chitosan can be used as an adsorbent for different types of dyes. However, adsorption capacity mainly depends on the nature of dye molecule, its molecular structure, degree of deacetylation and other experimental conditions like pH, temperature, contact time, etc.

10.4 Modified Chitosan

Chitosan exhibits great potential as adsorbent for toxic dyes, but at the same time it suffers from the drawback of low mechanical strength and poor acid stability. These two criteria are important for translating the use of chitosan as an adsorbent at industrial scale where rigidity of the structure and chemical environment are important considerations. Physical modification of chitosan is known to be an effective way to reinforce improved mechanical property and also acid stability. Chitosan can be physically transformed into various forms like beads, membranes, fibres, hydrogel or granules. Similar to the chitosan flakes, physically transformed chitosan also exhibits excellent dye adsorption properties with enhanced stability. The presence of reactive hydroxyl and amino functional groups in chitosan facilitates the modification process. Physical modifications do not bring any chemical change in the chitosan but bring in different morphological changes such as varying porous structures of chitosan with improved adsorption capacity. Physical modification causes expansion of chitosan chains, reduces crystallinity and increases the rate of diffusion of dye molecules to the internal adsorption sites (Li and Hsieh 2006). Porous chitosan beads can be prepared by the dropwise addition of acidic solution of chitosan into NaOH solution (Bekçi et al. 2008). It is important to thoroughly wash the beads with distilled water to remove any traces of NaOH from the surface. These dried chitosan beads exhibited excellent adsorption characteristics towards removal of cationic malachite green dye at higher pH. The favourable adsorption is attributable to interaction of dye molecules with the lone pair of electron present on nitrogen atom of the dye structure. Furthermore, as the adsorption is better at higher pH, so the surface of the chitosan could be modified by hydroxyl ions and hence favoured electrostatic interaction with the cationic dye. This is corroborated from the adsorption data at lower pH which revealed poor adsorption capacity owing to electrostatic repulsion between cationic dye and protonated chitosan beads. Chitosan beads were also effective in the removal of anionic dyes such as eosin Y, from aqueous solution (Chatterjee et al. 2005). Adsorption studies suggested that the removal of anionic dyes by chitosan beads follows pseudo-second-order kinetics and satisfies Langmuir model with a high adsorption capacity of 80.84 mg/g at 30 °C and at pH 4. Further, it was also illustrated that the 98% of the adsorbed eosin Y can be de-adsorbed from the chitosan beads at pH 11 or 12. The recycled chitosan beads can be reused as adsorbent for eosin Y dye up to five cycles without any significant loss in adsorption capacity.

Physical modification of chitosan in the form of membrane or film is another effective way to increase the adsorptive property by increasing porosity of the material. Different types of chitosan membranes are being developed by simple casting method on glossy paper surface (Mello et al. 2006). These types of chitosan membranes were very efficient in retaining methylene blue dye molecules with 100% efficiency. Similarly, the dye adsorption capacity of chitosan films prepared on plexiglas plates was compared with that of raw chitosan powder (Moura et al. 2016). It was found that chitosan films with 95% degree of deacetylation exhibited 99% adsorptive removal of reactive black 5 dye at pH 4. The advantage of using chitosan films as adsorbent is the ease in the separation and recovery of the adsorbent from the dye solution so that the film can be reprocessed for multiple uses.

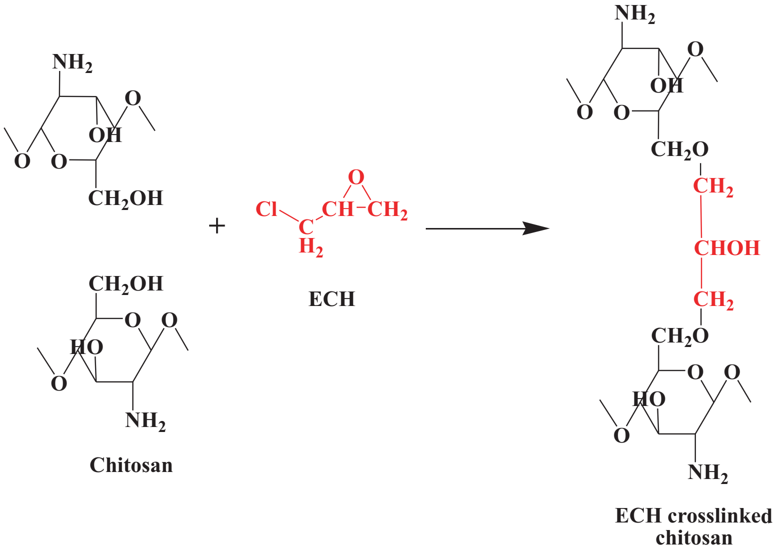
Chitosan in the form of fibres is also found to be promising adsorbent for the adsorption of coloured dye stuff as impurities from wastewater. Chitosan fibres are cheaper and exhibit superior adsorption characteristics as compared to activated carbon fibres (Yoshida et al. 1991). Pure chitosan nanofibres of varying diameter were successfully synthesized using electrospinning method (Li et al. 2018a, b). The electrospinning parameters have a significant effect on the specification of the nanofibres. It is found that the average diameter of chitosan fibre was about 100 nm, which increased by about 30% when the operating voltage of the electrospinning unit was decreased from 20 kV to 15 kV. Further, the feed chitosan concentration is also important in controlling the diameter of the fibres. This is attributable to the viscosity of the chitosan feed. For example, the average diameter of the fibres was increased to 164 nm, when chitosan concentration was raised from 6 to 7% w/v. The dye adsorption efficiency of chitosan nanofibres is also influenced by its diameter. It was observed that dye adsorption capacity decreased with increase in the fibre diameter. This can be attributed to increase in surface area due to decreasing fibre diameter. High adsorption capacity of 1377 mg/g was achieved with chitosan fibres with an average diameter of 80–100 nm. The observed adsorption properties are superior to microscale chitosan sample prepared using traditional thermal-induced separation technique. As-prepared microstructures consist of laminar films and inter-connective pores which revealed an adsorption capacity of 412 mg/g only. Hollow chitosan fibres prepared via dry–wet spinning methods were also tested as a suitable bio-adsorbent for the removal of reactive blue 19 dye (Mirmohseni et al. 2012). It was observed that the dye uptake by the hollow fibres follows pseudo-second-order kinetics and obeys Freundlich isotherm. A high adsorption capacity of 454.5 mg/g was achieved at pH 3.5 in 90 min.

Similarly, porous chitosan nanofibers were fabricated by electrospinning method using 82.5 wt% deacetylated chitosan blended with polyvinyl alcohol (PVA) (Li and Hsieh 2006). The chitosan/PVA composition was important factor for obtaining lump less uniform nanofibers of desirable average diameter, which varied in the range of 20–100 nm. Hydrolysis of these chitosan nanofibres with NaOH resulted into nanoporous fibres with non-uniform surface morphology and pores. The porous structure in chitosan nanofibres was achieved by removing PVA matrix by alkali treatment. Further, the stability of the chitosan nanofibres was improved by cross-linking chitosan fibre with Denacol EX841. These types of cross-linked chitosan nanofibres exhibited efficient adsorptive removal of acid dye (Yoshida et al. 1993). The maximum amount of acid orange II dye was adsorbed at pH 6.9 was10.6 mol/kg on chitosan nanofibres crosslinked with 4.76 wt% Denacol EX841. Chitosan fibres were also employed for the recovery of direct dye and acid dye from dilute aqueous solution. Therefore, it can be affirmed that porous chitosan was an excellent strategy for removing dye via adsorption.

10.5 Cross-Linked Chitosan Beads

Though chitosan exhibits great potential as a dye adsorbent, it also suffers from several limitations. High crystallinity and low hydrophilicity and porosity are some of the major shortcomings associated with chitosan. Intra-/intermolecular hydrogen bonding between hydroxyl and amine groups of same/different chains would tend to reduce the dye adsorption capacity of chitosan due to the unavailability of the functional groups for binding with dye molecule. Chemical structure of dyes also affects the adsorption properties of cross-linked chitosan beads (Cestari et al. 2004). The adsorption of dye on the surface of chitosan beads occurs in two steps, i.e. transfer of dye molecules from aqueous phase to the surface of adsorbent followed by the diffusion of molecule into the interior pores and binding sites. Dye removal by chitosan beads depends upon the concentration and nature of binding functional groups on dye. Intramolecular hydrogen bonding between the sulfonic acid and NH_2 groups of dye hinders its adsorption on the chitosan beads due to the absence of electrostatic forces. Similarly, more ramified and branched structure of dyes would also suppress the adsorption process at high temperatures. This is because at high temperature desorption is more favourable as compared to adsorption due to bulky dye structure. On the other hand, for linear and small dye molecules, adsorption increases with increase in temperature. This is due to opening of the pores of the adsorbent which helps in the diffusion of dye molecules to the internal binding sites those available on the beads.

Notably, bulky dye molecules might not be favourable to penetrate into the complex porous structure of chitosan due to steric hindrance. In this regard, modification of chitosan into gel beads by cross-linking agent is found to drastically enhance its adsorption capacity. Cross-linking of chitosan resulted in improving some of the important specifications for enhanced dye adsorption, e.g. improving mechanical strength and its stability in acidic medium and increasing porosity as well as increasing surface area. In addition, diffusion of dye molecules into the internal sorption sites of chitosan beads has been accounted for 99% malachite green (cationic) dye removal efficiency at pH 8 (Guibal et al. 2005). Several cross-linking agents, e.g. epichlorohydrin (ECH), sodium tripolyphosphate (TPP), glutaraldehyde (GLA) and ethylene glycol diglycidyl ether (EGDE), revealed better results in preparing chitosan beads.

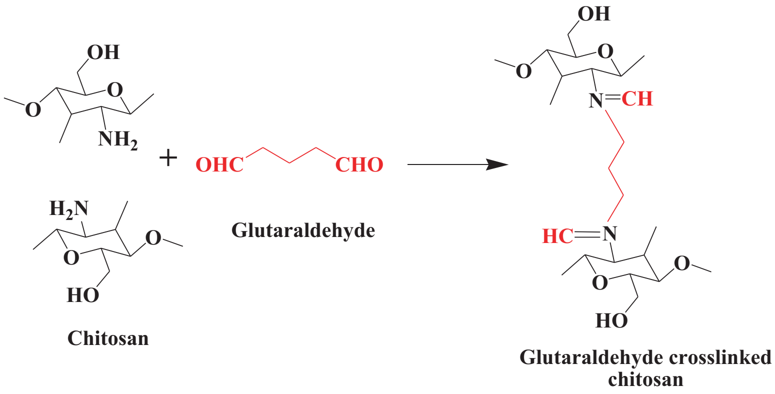


Scheme 10.1 Mechanism of chitosan cross-linking by epichlorohydrin (ECH)

10.5.1 *ECH Cross-Linked Chitosan*

The ECH has highly reactive chlorine centre and an oxirane ring. The cross-linking of chitosan by ECH occurs through the hydroxyl group of chitosan, as shown in Scheme 10.1. Because of this the amine group of chitosan remains free for adsorption with dye molecule. It is observed that smaller-sized ECH-linked chitosan beads could remove reactive red 189 dye from aqueous system at acidic pH. The corresponding adsorption capacity was 1936 g/kg, which is much better than pure chitosan as adsorbent at acidic pH (Chiou and Li 2002). Furthermore, successful studies on the removal of several other anionic dyes such as reactive red 222, acid blue 92 and reactive black 5 are also reported using ECH cross-linked chitosan beads as adsorbent (Chiou et al. 2003, Hanh et al. 2007, Kim et al. 2012).

In addition, ECH cross-linked chitosan beads were developed in acidic and basic medium for adsorption of azo dye (Li et al. 2013). Under similar adsorption conditions and at pH 4, strikingly better adsorption of Congo red (anionic azo dye) was found than the cationic dye. This is attributable to electrostatic interactions between positive residual charge at the amine groups of cross-linked chitosan and negatively charged dye molecules. On the same ground, the poor adsorption of cationic dye was due to electrostatic repulsions between the positively charged adsorbent and cationic dye molecules. Further, it is found that ECH cross-linked chitosan prepared in alkaline medium exhibited higher adsorption capacities than the unmodified chitosan.



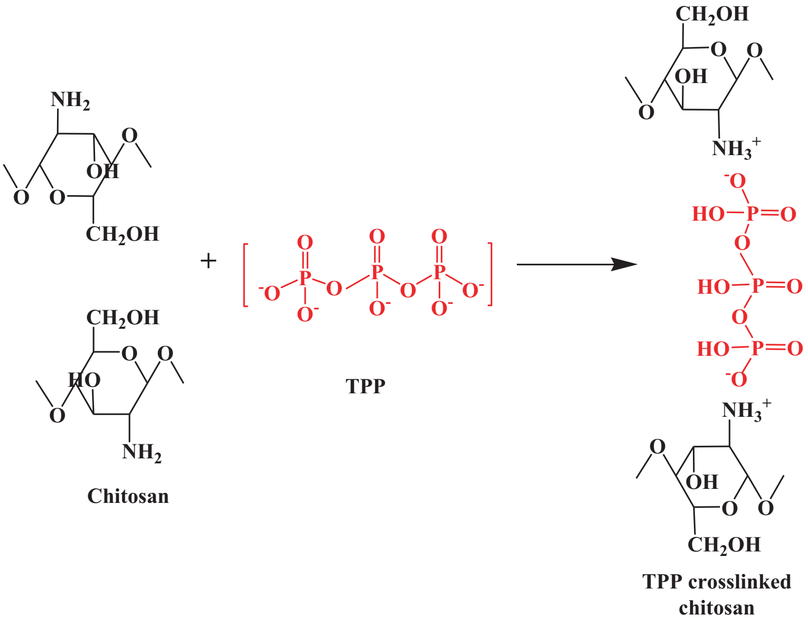
Scheme 10.2 Cross-linking mechanism of chitosan by glutaraldehyde

10.5.2 GLA Cross-Linked Chitosan

Glutaraldehyde (GLA) has been another interesting cross-linking agent for developing chitosan beads. GLA contains two aldehyde groups which cross-link with the amine group of chitosan through N=C linkages, as shown in Scheme 10.2. Because of this, the hydroxyl groups in chitosan become available for interacting with the dye molecules for adsorption. The effective cross-linking of chitosan with GLA in solution phase takes has been optimized to be a slow process (Guibal et al. 2003). Several studies have been reported on adsorptive removal of dye molecules from aqueous solution by chitosan beads cross-linked with GLA. For example, efficient adsorption of methyl orange (an anionic azo dye) by GLA cross-linked chitosan beads suggested affinity of anionic dye by positive residual charge on chitosan beads via electrostatic interactions (Morais et al. 2008). However, it is observed that GLA cross-linked chitosan beads are less efficient for adsorptive dye removal than other types of chitosan beads (Kamari et al. 2009). This could be attributed to the masking of the active binding sites, i.e. $-NH_2$ groups on chitosan during cross-linking.

10.5.3 TPP Cross-Linked Chitosan

Tripolyphosphate is a polyanionic molecule which can cross-link with the protonated amino group of chitosan in acidic condition (Liu et al. 2004). A tentative mechanism of cross-linking is shown in Scheme 10.3. The anionic TPP binds with cationic chitosan polymer via inter-/intramolecularly and resulted in the successful bead formation (Crini and Badot 2008; Bhumkar and Pokharkar 2006). It is noted



Scheme 10.3 Mechanism of chitosan cross-linking by tripolyphosphate (TPP)

that the TPP cross-linked chitosan beads are more rigid as compared to chitosan beads prepared using ECH as cross-linker. The TPP cross-linked chitosan beads exhibited excellent pH-dependent adsorption of reactive red 189 dye from wastewater using TPP cross-linked chitosan beads (Chiou and Li 2003). The maximum dye adsorption capacity was 1800 mg/g at pH 3 and desorption occurred at pH 10.

Similarly, a comparison study on adsorption of Congo red anionic dye and methylene blue cationic dye was performed on TPP cross-linked chitosan beads (Kyaw et al. 2011). The adsorption efficiency was higher (~82%) for the Congo red dye at an optimum pH of 4. At the same pH and adsorbent dose, only 42% of methylene blue dye (cationic) was removed. This is governed by favourable/unfavourable electrostatic interactions between the charged pairs of adsorbent and dye molecule. Comparative studies of the adsorption of anionic Congo red dye on chitin and TPP cross-linked chitosan beads were performed in a wide pH range of 2–9 (Raval et al. 2016). Gradual decrease in the adsorption capacity values was observed with increased pH values. At high pH value of 7 and above, adsorption of dye on both the adsorbent is suppressed due to the presence of excessive hydroxyl ions which compete for the available adsorption sites. Removal of acid green 27 dye from aqueous solution was achieved using nanometre size TPP cross-linked chitosan beads (Hu et al. 2006). The maximum monolayer adsorption capacity was determined to be 1051.8 mg/g. It was further concluded that the nanosized chitosan beads displayed significantly higher adsorption capacity as compared to micron-sized chitosan beads due to high surface area.

Furthermore, molecular structure of dye also affects the adsorption capacity of TPP cross-linked chitosan beads significantly (Chiou and Chuang 2006). For example, the complexity in the molecular structure of reactive blue 15 dye resulted in its poor adsorption as compared to small linear structure of methanol yellow dye. However, ECH cross-linked chitosan beads revealed better adsorption efficiencies as compared to TPP cross-linked chitosan beads. If we compare the structure of ECH cross-linked and TPP cross-linked chitosan beads, it is evident that amine groups are available for binding in ECH cross-linked beads while hydroxyl groups are available in TPP cross-linked chitosan beads. It is also implied that the amine groups are better sites for dye adsorption than the hydroxyl groups in the chitosan beads.

10.5.4 Other Cross-Linking Agents

EDGE is an important cross-linking agent which contains two epoxide functional groups at the edges. EDGE cross-linking provides mechanical strength and acid stability to the chitosan and reduces swelling ability (McCloskey et al. 2009). Comparative study of the adsorption of acid red 37 (AR 37) and acid blue (25) from aqueous solution was performed using chitosan and EDGE cross-linked chitosan as adsorbents. It was found that chitosan exhibits much better adsorption properties for the two dyes as compared to its cross-linked derivative. This could be due to the possible cross-linking of the EDGE with $-NH_2$ groups of chitosan via epoxide groups, which reduces the concentration of available active binding sites. The adsorption profile matched well with the Langmuir and pseudo-second-order models. It has been also shown that both the adsorbents are capable of retaining their adsorption capacities even after three cycles of adsorption–desorption. Other cross-linked used for synthesizing chitosan beads are diglycidyl (7-ethyloctadecane diacid diglycidyl) (Shimizu et al. 2003), dimethyloldihydroxy ethylene urea (Fahmy et al. 2004) and ionic liquids (Naseeruteen et al. 2018).

10.6 Grafted Chitosan

Grafting is an effective way of enhancing adsorption capacity of chitosan without altering its properties. Grafting brings physical as well as chemical modifications in chitosan and improves its mechanical strength. As mentioned earlier, chitosan backbone has hydroxyl and amine functionalities which act as reaction centres for grafting. Grafting of different functional groups in chitosan occurs via formation of covalent bonds and has no significant effects on its biocompatibility, biodegradability and mucoadhesivity. On the other hand, grafting could introduce new functional groups in chitosan structure to enhance the concentration of active sites for binding of dye molecules and also control its diffusion properties (Crini and Badot 2008). There are many routes of synthesizing grafted chitosan, but the most common among them is free-radical polymerization. Ammonium persulfate (APS), potassium persulfate (PPS), ceric ammonium nitrate (CAN), thiocarbonate–potassium bromate (TCPB), potassium diperiodatocuprate (III) (PDC), 2,2-azobisisobutyronitrile (AIBN) and ferrous ammonium sulphate (FAS) are some of the examples of initiators that have been used to initiate grafting copolymerization. In this strategy, the mechanical and adsorptive capability of chitosan was improved by cross-linking, and the grafting further augmented the adsorption capability. It is further noted that the resultant properties of the grafted chitosan depend on the molecular structure, length, concentration and properties of the side chain (Jayakumar et al. 2005). For example, adsorptive removal of reactive dye effluent was enhanced for the batch of chitosan beads prepared by amine-grafted GLA and ECH as cross-linking agents (Kyzas et al. 2011). Adsorption capacity of grafted chitosan is also influenced by the amount of grafting reagent. Therefore, it is necessary to optimize the concentration of grafting agent to achieve maximum number of active binding sites (Kyzas et al. 2013). Acrylamide and poly(ethyleneimine) were successfully employed as reagents for the grafting of amido and imino functional groups, respectively. Furthermore, the adsorption capacity of poly(ethyleneimine)-grafted chitosan was found to be better than that of acrylamide-grafted chitosan. This is attributable to more electropositive character of imino groups as compared to amido groups. The adsorption capacity of chitosan grafted with poly(ethyleneimine) enhanced the adsorption capacity by a factor of 3.5. Similarly, ethylenediamine grafting also increases the amino group concentration on chitosan surface which causes high removal efficiency of anionic dyes from wastewater (Huang et al. 2011).

10.7 Chitosan Composites

Chitosan has been widely used for synthesizing composites including those with nanoscale materials. For example, clay, activated clay, charcoal and graphene oxide and different types of metal oxides are only some of the materials with which chitosan composites were made to derive better adsorptive properties. Notably, the materials listed above are also well known adsorbents for removing wide range of hazardous compounds including dyes. Therefore composites of these materials with chitosan have often resulted in achieving improvement in adsorption properties. These types of chitosan-based composites are found to offer improved mechanical and chemical stability with large surface area, which made them desirable adsorbent for large-scale dye removal treatment. Some of the chitosan-based composites as adsorbents are discussed below.

10.7.1 Chitosan–Clay Composites

Similar to chitosan, clay minerals have also received much attention in the removal of pollutants from aqueous solution via adsorption mechanism. Integration of chitosan with clay material led to the development of more efficient adsorbent system. The composition of chitosan and clay would play important role in the morphology as well as the adsorption properties of the composites. Chitosan-activated clay beads of diameter 4.42 mm were synthesized using a mixture of NaOH and ethanol (Chang and Juang 2004). These composite beads exhibited better adsorptive removal of methylene blue and reactive red 222 dye from water, as compared to activated clay. The highest adsorption capacities of chitosan-activated clay composites as determined from the Langmuir adsorption isotherm were 330 g/kg and 1912 g/kg for methylene blue and reactive red 222 dyes, respectively. The adsorption capacities of the composites were either better or similar to those of the chitosan beads. Under such circumstances, the advantage of using clay–chitosan beads would limit the use of chitosan which is more expensive than clay. Consequently, the cost of dye removal could be drastically reduced by using optimized composition of clay and chitosan. In addition, the chitosan-clay composite beads exhibit excellent mechanical strength and hence these composites could be repeatedly used under harsher physical conditions. The mechanisms of the dye adsorption were different as the reactive red 222 dye adsorption obeyed pseudo-first-order kinetics, whereas methylene blue dye adsorption followed pseudo-second-order kinetics. The reason for the difference in the adsorption kinetic mechanism is attributed to the difference in the molecular structures of dyes. Small methylene blue dye molecules can easily migrate into the interior pores of the adsorbent beads and thus follow diffusion mechanism. Fixed-bed adsorption of methylene blue dye was carried out using beads composed of modified ball clay and chitosan, of particle size in the range 0.5–20 mm (Auta and Hameed 2014). Beads of modified ball clay and chitosan composite adsorb molecules of methylene blue dye at high pH via electrostatic forces. At high pH value, OH^- ions abstract proton from the active sites of the composite adsorbent such as SiOH, COOH, etc. and bind with dye molecules. At low pH values, protonation of these functional groups is not favorable for adsorption of dye molecules on the surface of adsorbent beads. The effect of inorganic salts such as sodium sulphate, sodium chloride and sodium bicarbonate were found to affect the uptake of dye molecules from aqueous solution. It was noted that the dye uptake was greatly hindered in the presence of sodium sulphate as compared to those of sodium chloride and sodium bicarbonate.

Bentonite and montmorillonite are some of the natural clay materials which are abundant in nature. They mainly consist of aluminium phyllosilicate mineral and are widely used as adsorbent for the removal of pollutants from wastewaters due to their low cost. Chitosan/montmorillonite nanocomposites were prepared with varying molar ratios of reactant materials and were explored as adsorbent for the removal of anionic Congo red dye (Wang and Wang 2007). Compared to pure chitosan and pure montmorillonite, these composites exhibited improved adsorption characteristics over a wide pH range of 4–9. Similarly, chitosan/bentonite composites have been widely used as adsorbent for the adsorption of toxic textile dyes from aqueous system (Dotto et al. 2016). Bentonite is an attractive support material for the immobilization of chitosan and is used to enhance its mechanical stability. Chitosan/bentonite composites also exhibited high adsorption efficiency and excellent acid stability. Chitosan/bentonite composites have been considered as a potential adsorbent for the removal of anionic and cationic dyes with easy phase separation and reusability. The maximum adsorption capacity achieved for anionic amaranth red and cationic methylene blue dyes from coloured effluents were 362.1 mg/g and 496.5 mg/g, respectively. In addition, chitosan/bentonite composites further cross-linked with glutaraldehyde have also been developed as adsorbent for the removal of Amido Black 10B anionic dye (Liu et al. 2015). The maximum adsorption capacity of such composite adsorbent was determined as 323.6 mg/g at 293 K and pH 2. Higher adsorption capacity of 418.4 mg/g was achieved for Amido Black 10B dye by Zr(IV) surface-immobilized, cross-linked chitosan/bentonite composites (Zhang et al. 2016a, b). Adsorption studies were also reported on the removal of weak acid scarlet dye using composites of chitosan and CTAB-modified bentonites (Guo et al. 2012). The active functional groups present in chitosan and bentonite or montmorillonite interact with each other to form grafted copolymer. Since some cross-linking agent is used for the grafting mechanism, the resultant polymer network comprises of free functional moieties at the end of the polymer chain which facilitates dye adsorption.

10.7.2 Carbon–Chitosan Composites

Activated carbon and graphene or graphene oxides are interesting carbonaceous materials and are known to be excellent adsorbent owing to high surface area porous structure. Compared to graphene, activated carbon is a low-cost material. But the adsorption capacities of these materials are usually very high and hence the cost of adsorbent can be compensated (Tan et al. 2008). Activated carbon can be prepared from any carbon-rich materials. For example, municipal waste, household kitchen waste and agricultural wastes can be treated to synthesis bulk amount of activated carbon (Ahmed 2016). ECH is found to be an excellent linker agent for developing activated carbon–chitosan composite beads (Auta and Hameed 2013). Fixed-bed adsorption studies of such activated carbon–chitosan composite beads exhibited excellent adsorption properties for the removal of cationic methylene blue dye and anionic acid blue 29 dye. Maximum adsorption capacities achieved in case of cationic methylene blue dye and anionic acid blue 29 dye by cross-linked chitosan beads were 103.64 and 193.4 mg/g, respectively, at 30 °C. This value has been increased to 197.3 and 345.1 mg/g when studies were conducted using activated carbon–chitosan composite beads. It has been demonstrated that microwave heating could reduce the time needed for synthesizing such activated carbon–chitosan beads (Chen and He 2017). The adsorption capacities of the composite bead increases with increasing activated carbon content attain a maximum adsorption capacity value of 35.4 mg/g with a 10:4 mass ratio of chitosan to activated carbon.

Graphene is a flat two-dimensional allotrope of carbon composed of sp^2 hybridized carbon atoms arranged in honeycomb-type structure. However, it is hydrophobic in nature and hence their application in aqueous medium would be challenging. This can be overcome by modifying and by oxidizing the peripheral carbons of the graphene system to synthesis hydrophilic graphene oxide. Essentially graphene oxide is easy to synthesize by Hummer's method or by modified Hummer's method (Verma and Dutta 2015). It should be realized that graphene oxide is highly soluble in water, and hence it may not be very convenient to be used as a heterogeneous adsorbent. It that case, either, graphene oxide can be used for functionalizing any material to be used as an adsorbent, e.g. clay and chitosan, for improving their adsorption property. In addition, graphene oxide can be reduced to amines and then its composite with clay can be more functional for adsorption. These derivatives of graphene systems can be categorized on the basis of different concentrations of oxygen functional groups such as –COOH, −OH and C−O−C in the basal plane and at the edges of graphene skeleton. Graphene surface can be chemically tuned for the removal of metal ions as well as dyes from aqueous solution (Verma and Dutta 2017a, Verma and Dutta 2017b). The composite of graphene oxide and chitosan can be synthesized by the formation of amide bond via reaction between –COOH group of graphene oxide and $–NH_2$ group of chitosan. In addition, glutaraldehyde is also known to act as a linker for synthesizing graphene-chitosan composites (Travlou et al. 2013). The functional groups of graphene derivatives and those in chitosan together act as active binding sites for the removal of dye molecules from solution. The adsorption efficiency of such graphene oxide/chitosan composites against the removal of reactive black 5 dye was very high (277 mg/g) at 25 °C and at pH 2. The dye adsorption was attributed to hydrogen bonding interactions between amine groups of chitosan and oxygen containing functional of graphene oxide. Further, it was noted that the adsorption capacity of the composite was better than those of individual materials used in making the composites. It should be remarked here that different morphologies of graphene oxide/chitosan composites were developed for dye adsorption application. The chitosan/graphene oxide hydrogel nanocomposites prepared by self-assembly and chitosan/graphene oxide fibre nanocomposites revealed excellent dye adsorption properties (Li et al. 2014; Chen et al. 2013). Dye adsorption due to interaction between the sulfonic acid ($–SO_3H$) group of dye molecule and the protonated amines of chitosan at acidic condition is discussed here.

10.7.3 Chitosan-Metal Oxide Composites

Metal oxides are versatile materials and some of them have found application as adsorbent. The ease of synthesis and extraordinary physico-chemical properties including high surface area of metal oxide nanoparticles are some of the key features for utilizing these materials as dye adsorbent. In addition, metal oxides exhibiting magnetic property are useful for the post adsorption magnetic separation from adsorbate medium. Further, it is observed that the adsorption properties of metal oxides are drastically improved when they are made composites with chitosan. For example, magnesium oxide nanoparticles immobilized on chitosan substrate were found to be an excellent adsorbent for the removal of methyl orange dye (Haldorai and Shim 2014). The advantage of immobilizing MgO nanoparticles on chitosan over free MgO nanoparticles is the ease of separation of the adsorbent after adsorption. In addition, the surface charge of chitosan/MgO nanocomposite was +50.7 mV at pH 7, which facilitated the removal of negatively charged dye molecules from solution by electrostatic interaction. It was possible to achieve 98% dye removal efficiency in 30 min with 0.5 g of chitosan/MgO nanocomposite. The scope for reusability of the chitosan/MgO nanocomposite has also been demonstrated up to five cycles without sacrificing its dye removal efficiency.

Similarly, $Fe(OH)_3$-loaded chitosan beads were developed for removal of anionic Congo red and methyl orange dyes from the solution (Li et al. 2018a, b). The adsorption capacities were 445.32 and 314.45 mg/g for Congo red and methyl orange, respectively, at pH 3. Such high adsorption capacities were attributed to positive surface charge on the adsorbent owing to protonation of the amine groups of chitosan. The dye adsorption mechanism was proposed on the basis of physical (electrostatic) and chemical interactions. The chemical interaction was discussed in the light of possible complexation mechanism based on hydrogen bonding or Lewis acid-base mechanism between $Fe(OH)_3$ and the dye molecules. In addition, magnetic composites of chitosan were prepared by incorporating Fe_3O_4, Fe_2O_3, $NiFe_2O_4$, $CoFe_2O_4$, $CuFe_2O_4$ and $ZnFe_2O_4$ particles (Haldorai et al. 2015; Zhu et al. 2010; Sadrolhosseini et al. 2017; Zhang et al. 2014; Ansari et al. 2016; Kumar et al. 2018). These magnetic nanocomposites showed fast dye adsorption properties with high efficiency. Also, presence of magnetic material in the composite provided an easy way of adsorbent separation using an external magnetic. Dye adsorption studies were also reported using ethylenediamine- and glutaraldehyde-modified magnetic chitosan nanoparticles (Zhou et al. 2011; Zhou et al. 2014). Furthermore, magnetic nanoparticles were also introduced in chitosan/graphene oxide composites to induce magnetic properties to the composites. This three-component adsorbent system was investigated for the adsorption of anionic and cationic dyes such as methylene blue (Fan et al. 2012b), methyl blue (Fan et al. 2012a) and methyl violet and alizarin yellow R (Gul et al. 2016). Langmuir adsorption capacities recorded for these studies were 180.83, 95.16, 17.66 and 14.82 mg/g, respectively. It was found that adsorption of anionic and cationic dyes by Fe_3O_4 supported chitosan/graphene oxide composite is not affected by the ionic strength of the solution. It was also studied that the as-prepared adsorbent can be reused up to four consecutive cycles without any loss in the adsorption capacity when acetone was used as the desorbing agent (Gul et al. 2016).

It should be remarked here that nanocomposites of chitosan and ZnO or TiO_2 or CuO offer very interesting property. These metal oxides are known to be excellent photocatalytic agent (Nenavathu et al. 2018; Fujishima et al. 2008, Sharma and Dutta 2015). So their nanocomposites or beads with chitosan could offer adsorptive photocatalytic degradation. Our ongoing studies on removal of Congo red anionic

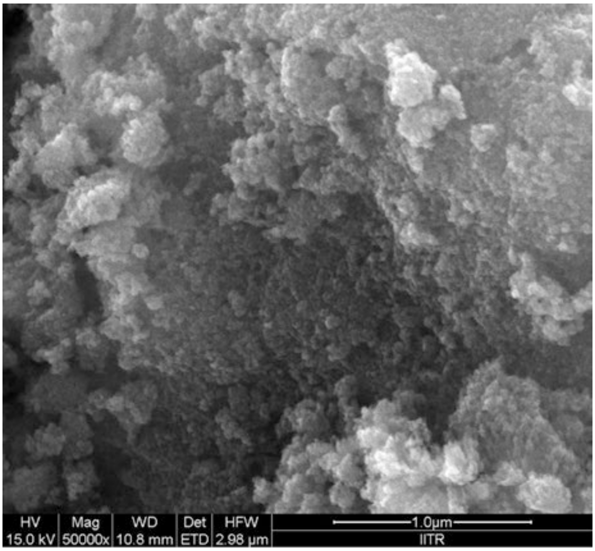


Fig. 10.3 FE-SEM image of ZnO–chitosan nanocomposite

dye by ZnO–chitosan nanocomposites under UV light exposure (λ = 365 nm) revealed initial adsorption of the dye on the surface of ZnO–chitosan nanocomposites followed by photocatalytic degradation of the dye. Here the ZnO–chitosan nanocomposite was prepared by hydrothermal method (Liu and Zeng 2003), where the initial chitosan composition taken was 5 wt % of the Zn precursor. The morphological information of the ZnO–chitosan nanocomposite is evident from the FE-SEM image (Fig. 10.3), showing spherical nanoparticles of ZnO adhered to the chitosan polymeric matrix. The synthesis of ZnO–chitosan nanocomposite was confirmed from XRD measurement which revealed formation of wurtzite structure (Fig. 10.4), and our results matched well with the XRD of ZnO reported in literature (Dutta et al. 2012). The band structure of ZnO is revealed from the UV-vis spectrum showing excitonic peak at 367 nm (Fig. 10.5). The dual role of adsorption and photocatalytic dye degradation by ZnO–chitosan nanocomposite was established by following decrease of the dye concentration in reaction medium, as shown in Fig. 10.6a. The decrease in the dye concentration in dark condition is due to adsorption process, where 58% of the dye molecules were adsorbed at equilibrium condition attained in 90 min. In this study, the dye concentration was deliberately kept high with respect to the amount of adsorbent in order to establish both adsorption and photocatalytic processes. The dye removal due to adsorption process and not due to photocatalytic process was ensured by treating the Congo red dye solution with ZnO–chitosan nanocomposite in dark condition. This corresponded to 58% dye removal in 120 min. Subsequently, when the reaction assembly was transferred to UV light exposure, a total of 96% of the dye molecules was removed (Fig. 10.6a). It should be mentioned here that the dye degradation during UV light exposure was not due to photolysis, which was confirmed from negligible decrease in dye concentration in a control study where the dye solution was exposed without treating with ZnO–chitosan nanocomposites. Therefore, the observed decrease in the dye

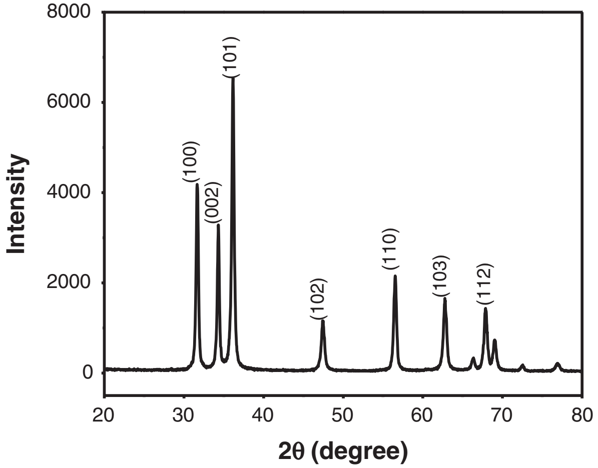


Fig. 10.4 X-ray diffraction of ZnO nanoparticles used in ZnO–chitosan nanocomposite

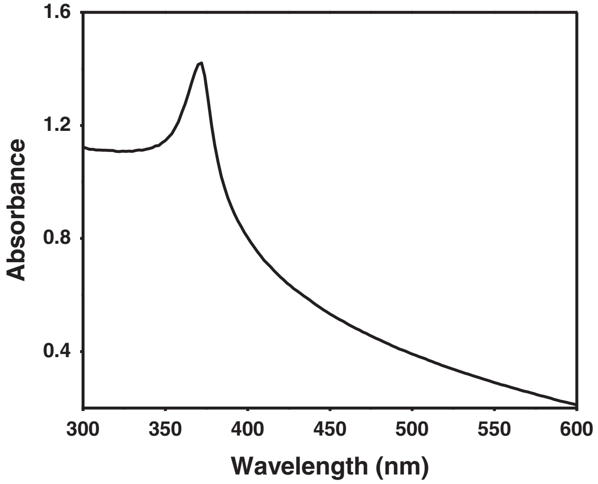


Fig. 10.5 UV-visible spectrum of ZnO nanoparticles used in ZnO–chitosan nanocomposite showing band structure

concentration under UV light after adsorption process was due to photocatalytic degradation triggered by ROS generation. Under UV light exposure, hydroxyl radicals are generated due to interaction of photoexcited holes at the valence band and moisture at the surface of the ZnO nanoparticles. Such phenomenon is very well documented by our research group (Nenavathu et al. 2013). Because of the degradation, the dye molecules were removed from the surface of the nanocomposites, and hence it was reused without any further dye desorption treatment. The reusability of the nanocomposite for three consecutive cycles of dye removal is shown in Fig. 10.6b.

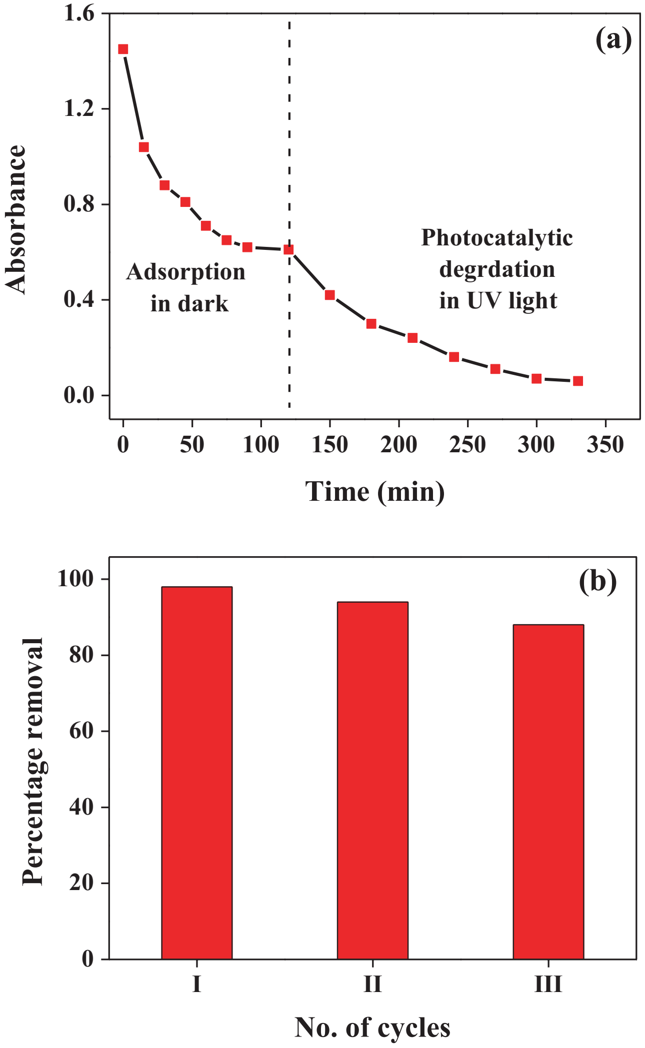


Fig. 10.6 (**a**) Dye removal efficiency of ZnO–chitosan nanocomposite via adsorption–photocatalytic degradation process and (**b**) reusability studies of ZnO–chitosan for dye removal

10.7.4 Other Chitosan-Based Composites

Novel chitosan composites were also prepared with other polysaccharide material such as cellulose which also exhibit great potential towards the removal of dye stuff from aqueous solution. The cellulose/chitosan composite showed a high Langmuir adsorption capacity of 381.7 mg/g at pH 7 and at 303 K for anionic Congo red dye (Wang et al. 2018). Adsorption property of nanofibrillated cellulose/chitosan composites modified with ethylenediamine was also evaluated against cationic and anionic dyes. The models cationic and anionic dyes considered for this study were methylene blue and new coccine, respectively (Liu et al. 2016). A high adsorption value of 0.67 mmol/g was observed for methylene blue dye at pH 4, whereas a value of 0.172 was observed at pH 2 for anionic new coccine dye. The reusability results showed that the effective desorption of dyes can be achieved using NH_4OH/NH_4Cl as desorbing agent. It was observed that after three cycles, the recycled adsorbent can keep 10% and 98% adsorption capacities for methylene blue and new coccine, respectively. The reason for the different adsorption capacities is attributable to the dissimilar adsorption mechanism of cationic and anionic dyes by ethylenediamine-modified nanofibrillated cellulose/chitosan composites.

Composites of chitosan pyrrole and chitosan aniline were also prepared with agricultural waste material such as rice bran and employed for the adsorption of malachite green dye. The respective adsorption capacities were 122.5 and 55 mg/L for an initial dye concentration of 200 mg/L with an adsorbent dose of 0.05 g/L (Bhatti et al. 2017). Other work also reports successful removal application of dyes by porous chitosan/hydroxyapatite composite membrane (direct blue 15, 369 mg/g) (Shi et al. 2017), cross-linked chitosan/β-cyclodextrin polymer composite (methyl orange, 392 mg/g) (Jiang et al. 2018), fly ash–chitosan–graphene oxide composite (acid red GR, 38.87 mg/g: cationic red X-5GN, 64.50 mg/g) (Sheng et al. 2016) and chitosan–alunite composite (reactive red 2, 462.74 mg/g: acid red 1, 588.75 mg/g) (Akar et al. 2016).

10.8 Other Aspects of Dye Adsorption on Chitosan-Based Adsorbents

The nature of the adsorption of adsorbate on the surface of adsorbent material is governed by thermodynamic parameters such as Gibb's free energy ($\Delta G°$), standard enthalpy change ($\Delta H°$) and standard entropy change ($\Delta S°$). These factors were further used to describe spontaneity, favourability and endothermicity/exothermicity of the adsorption process. Here, in this section, we will only consider the thermodynamic aspects of the dye removal studies using chitosan-based solvents discussed above. It was observed that the adsorptive removal dye by different forms of chitosan and its composites are spontaneous in nature as suggested from the negative $\Delta G°$ and is a favourable process. However, adsorption capacity of the chitosan-based adsorbent may increase or decrease with the rise of temperature. It was observed that the endothermicity/exothermicity of the adsorption process is independent of the chemical nature of dye. Most of the studies discussed above revealed that the adsorption of dyes by unmodified chitosan is an endothermic process. The reason for the enhancement in the adsorption capacity values is the diffusion of dye molecules into the interior of the adsorbent material at high temperature. Thermodynamic studies of the adsorption of acidic dyes on chitosan composites with montmorillonite, bentonite, $Fe(OH)_3$, cellulose and fly ash–graphene oxide are endothermic in nature (Wang and Wang 2007; Liu et al. 2015; Li et al. 2018a, b; Wang et al. 2018; Sheng et al. 2016). On the other hand, endothermic as well as exothermic adsorption processes were reported for the removal of reactive dye by ECH cross-linked chitosan (Kim et al. 2012; Chiou and Li 2003). The reason for the variation in the adsorption thermodynamics may depend on the structural difference of the adsorbent material.

Kinetics of the adsorption of different types of dyes by chitosan and its composite material follows pseudo-second-order kinetics rather than pseudo-first-order kinetics. However, very few studies report some special conditions where the adsorption kinetics follows pseudo-first-order model or any other kinetic model such as Elovich kinetic model (Chiou and Chuang 2006; Dotto et al. 2016). The kinetics of the adsorption process also depends on the initial dye concentration. It was found that the adsorption of anionic metanil yellow and reactive blue 15 dye on chemically cross-linked chitosan follows pseudo-first-order kinetics at low initial dye concentrations but follows pseudo-second-order model for higher initial concentration of dye (Chiou and Chuang 2006). The reason for the change in the kinetic mechanism lies in the fact that the adsorption driving forces are stronger for higher initial dye concentration. Hence it can be concluded that adsorption of dyes on chitosan-based adsorbent is independent of the nature of dye (cationic/anionic/reactive). But at the same time, its mechanism depends upon the experimental conditions.

10.9 Summary

This book chapter deals with the discussions on utilization of chitosan as a versatile adsorbent for removal of organic dyes from aqueous system via adsorption mechanism. A consolidated list of chitosan-based adsorbent for the removal of various types of dyes is presented in Table 10.1. Chitosan is derived by the deacetylation of its precursor material chitin by alkali treatment. The presence of free hydroxyl and amino groups in chitosan is helpful in the adsorption of dye molecules. Adsorption of anionic dyes by chitosan occurs at low pH values due to protonation of its functional groups. Removal of cationic dyes by chitosan yields low adsorption capacity values due to the electrostatic repulsive force between protonated chitosan and positively charged dye molecules. Adsorption capacity of chitosan is greatly affected by the degree of deacetylation, crystallinity and pH of the dye solution. Some other drawbacks associated with chitosan are its low mechanical strength and acid stability.

It is found that the adsorption capacity, mechanical strength and acid stability of chitosan can be improved by performing physical and chemical modifications of chitosan. Raw chitosan can be modified into various morphologies such as beads, fibres, membranes and nano- and microparticles. In addition, physical modifications of chitosan can lead to porous network structure with an advantage of reusability of the adsorbent. However, this type of modification is sometimes accompanied with

Table 10.1 Consolidated list of chitosan based adsorbent for dye adsorption

Sl. No.	Adsorbent	Dye	Adsorption capacity	Temperature (°C)	pH	References
1.	Chitosan	Astrazon GTLN red	58.82 mg/g	20	6	Pietrelli et al. 2015
		Telon B red	144.9 mg/g			
		Remazol RR gran yellow	98.04 mg/g			
		Scarlet red 23	142.8 mg/g			
2.	Chitosan	Acid green 25	645.1 mg/g	25	4	Wong et al. (2003)
		Acid orange 10	922.9 mg/g			
		Acid orange 12	973.3 mg/g			
		Acid red 18	693.2 mg/g			
		Acid red 73	728.2 mg/g			
3.	Chitosan 10B	Methyl orange	30.14 μmol/g	33	4	Saha et al. (2010)
4.	Chitosan hydrogel (DD = 90%)	Reactive black 5	1559.7 mg/g	22	4	Jóźwiak et al. (2017)
5.	Chitosan beads	Malachite green	93.55 mg/g	30	8	Bekçi et al. (2008)
6.	Chitosan hydrobeads	Eosin Y	80.84 mg/g	30	8	Chatterjee et al. (2005)
7.	Chitosan powder	Reactive black 5	654.3 mg/g	25	4	Moura et al. (2016)
8.	Chitosan film	Reactive black 5	589.5 mg/g	25	4	Moura et al. (2016)
9.	Chitosan nanofibrous membranes (86 nm)	Acid blue 113	1338 mg/g	RT	–	Li et al. (2018a, b)
10.	Chitosan hollow fibres	Reactive blue 19	454.5 mg/g	25	3.5	Mirmohseni et al. (2012)
11.	ECH cross-linked chitosan beads (2.3–2.5 mm)	Reactive red 189	1936 mg/g	30	3	Chiou and Li (2002)
12.	ECH cross-linked chitosan beads	Reactive red 222	2252 mg/g	30	3	Chiou et al. (2003)
13.	ECH cross-linked chitosan beads	Reactive black 5	0.68 mol/kg	35	5	Kim et al. (2012)

(continued)

Table 10.1 (continued)

Sl. No.	Adsorbent	Dye	Adsorption capacity	Temperature (°C)	pH	References
14.	GLA cross-linked chitosan beads	Acid blue 25	127.06 mg/g	27	4	Kamari et al. (2009)
		Acid blue 37	166.67 mg/g	27	6	
	H_2SO_4 cross-linked chitosan beads	Acid blue 25	102.53 mg/g	27	4	Kamari et al. (2009)
		Acid blue 37	139.28 mg/g	27	6	
15.	Chitosan beads	Congo red	166.67 mg/g	RT	6	Raval et al. (2016)
16.	Chitosan nanoparticles	Acid green 27	1051.8 mg/g	25	5	Hu et al. (2006)
17.	Cross-linked chitosan beads	Metanil yellow	1334 mg/g	30	4	Chiou and Chuang (2006)
		Reactive blue 15	722 mg/g			
18.	Chitosan ionic liquid beads A	Malachite green	8.07 mg/g	RT	4	Naseeruteen et al. (2018)
19.	EDA modified chitosan	Eosin Y	294.12 mg/g	25	5	Huang et al. (2011)
20.	Chitosan-activated clay composite	Methylene blue	330 mg/g	30	7.14	Chang and Juang (2004)
		Reactive dye RR222	1965 mg/g	30	6.47	
21.	Chitosan/ montmorillonite nanocomposite	Congo red	54.52 mg/g	30	7	Wang and Wang (2007)
22.	Chitosan/bentonite hybrid composite	Amaranth red	362.1 mg/g	25	2	Dotto et al. (2016)
		Methylene blue	496.5 mg/g	25	10	
23.	Cross-linked chitosan/ bentonite composite	Amido black 10B	323.6 mg/g	20	2	Liu et al. (2015)
24.	Chitosan–CTAB modified bentonites	Weak acid scarlet	102 mg/g	25	–	Guo et al. (2012)
25.	Graphene oxide/ chitosan fibres	Fuchsin acid dye	175.4 mg/g	20	4.5	Li et al. (2014)
26.	Ethylenediamine-modified magnetic chitosan nanoparticles	Acid orange 7	3.47 mmol/g	25	4	Zhou et al. (2011)
		Acid orange 10	2.25 mmol/g		3	
27.	Glutaraldehyde cross-linked magnetic chitosan nanoparticles	FD&C blue 1	475.61 mg/g	25	3	Zhou et al. (2014)
		D&C yellow 5	292.07 mg/g			

(continued)

Table 10.1 (continued)

Sl. No.	Adsorbent	Dye	Adsorption capacity	Temperature (°C)	pH	References
28.	Magnetic chitosan/ graphene oxide composite	Methylene blue	180.83 mg/g	30 ± 0.2	10	Fan, Luo, Sun, Li, Lu and Qiu. (2012)
29.	Magnetic chitosan grafted with graphene oxide	Methyl blue	98.52 mg/g	30	5.3	Fan, Luo, Li, Lu, Qiu and Sun (2012)
30.	Cellulose/chitosan hydrogel	Congo red	381.7 mg/g	30	7	Wang et al. (2018)

the lowering of adsorption capacity due to the screening of the active binding sites which hinders dye adsorption process. Chemical modifications of chitosan include modifications in its hydroxyl and amine functional groups to achieve high dye removal efficiency.

Another way of increasing adsorption capacity of chitosan is the formation of its composites with other adsorbent materials. Some of the commonly used materials that are used to reinforce adsorption capacity of chitosan include clays, activated carbon, graphene and its derivatives and metal oxide nanoparticles. The incorporation of these materials improves mechanical strength of chitosan and also increases its stability in acids. Incorporation of magnetic nanoparticles in chitosan provides as easier way of the magnetic separation of the adsorbent. Finally, it has been demonstrated that chitosan–metal oxide nanocomposite could be an excellent choice for the removal of dye molecules via adsorptive photocatalytic degradation, which has tremendous scope and future for translating the system to industrial level.

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Chapter 11

Ionic Liquid Modified Activated Carbon for the Treatment of Textile Wastewater

Tanvir Arfin, Neelima Varshney, and Bhawana Singh

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Abstract The dependency on water has increased three times more than the increase in population. It has led to a rise in health problems and has limited the development as well as the growth of the world in terms of agricultural and economy. It has become mandatory to treat the wastewater of textile industry and make it pure in order to meet the demands of the people in the future. Various treatment processes have also been applied to convert wastewater into a suitable form where the linking of the innovative technology-oriented process with the conventional process has proved to be appropriate. For the treatment of textile wastewater, the application of ionic liquid modified activated carbon has yielded fruitful results, showing good properties in terms of selectivity, stability and favourable adsorption

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T. Arfin (✉) · N. Varshney · B. Singh
Environmental Materials Division, CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), Nagpur, India

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capabilities in comparison with other materials. In the present book chapter, the significant ionic liquid modified activated carbon along with their uses for wastewater treatment is described.

Keywords Textile · Wastewater · Ionic liquid · Textile industries · Dye

11.1 Introduction

Textile is a fabric or a type of cloth which is made of filament or yarn. Textile is a flexible material consisting of a network of natural (wool, cotton, silk, etc.) and artificial (rayon, nylon, polyester, etc.) fibres. The word textile originates from the *Latin* word Taxtilis and the *French* word Texere, which means 'to weave,' and originally it means woven fabric. Textile is formed by different processes like knitting,weaving, crocheting, felting, tufting and knotting. Textile includes threads, ropes, cords, braids, embroidery, net and laces. Thus textile includes threads, ropes, cords, braids, embroidery, nets and laces. Basically *textile* is any material made of interlacing fibres, including *carpeting* and *geotextiles*. Textile production can be increased by industrialization and using some advanced techniques nowadays (Schwartz 2008).

The maximum amount of wastewater effluents is generated from the textile industry because of the application of water for various operations of wet processing. The effluents of such industry include substances such as dyes, acids and so on (Paul et al. 2012; Sharma et al. 2018). Hence, it has been observed that the textile industry uses high quantity of water in comparison with other industries that release even maximum pollutants as well. It is seen that the textile industry employs approximately 200 L of water per kg of fabrication process, every day (Ding et al. 2010). As per the estimation made by the World Bank, the dyeing and finishing work for fabrics are releasing about 17–20 % of effluents in terms of wastewater (Kant 2012).

In India, owing to the leading demands of cotton fabric and polyester, the consumption of dyes and its stuff is very high, nearly 80% of 1,30,000 tonnes (Naik et al. 2013). Such dyes lead to a severe hazardous impact on the photosynthetic activity within the plants. It also affects the aquatic life in terms of less light penetration and consumption of oxygen (Javadian et al. 2014). It is fatal to various marine organisms as it releases different metals and even chlorine which are dangerous. The suspended substances may choke the gills of the fish which may lead to death. It reduces the ability to make food and oxygen in the algae. The dyes are reported to be severe for even the municipal treatment of wastewater (Naushad et al. 2016; Sophia et al. 2019).

Currently, the heterocyclic and aromatic forms of dyes are applied in the industry. The complex and certain structural dyes are leading to complication in the degradation process in any form of matrix and wastewater (Ding et al. 2010). The toxic substance released from the textile industry and mineralization of dyes has become a challenging task and concern to overcome pollution (Arfin et al. 2019).

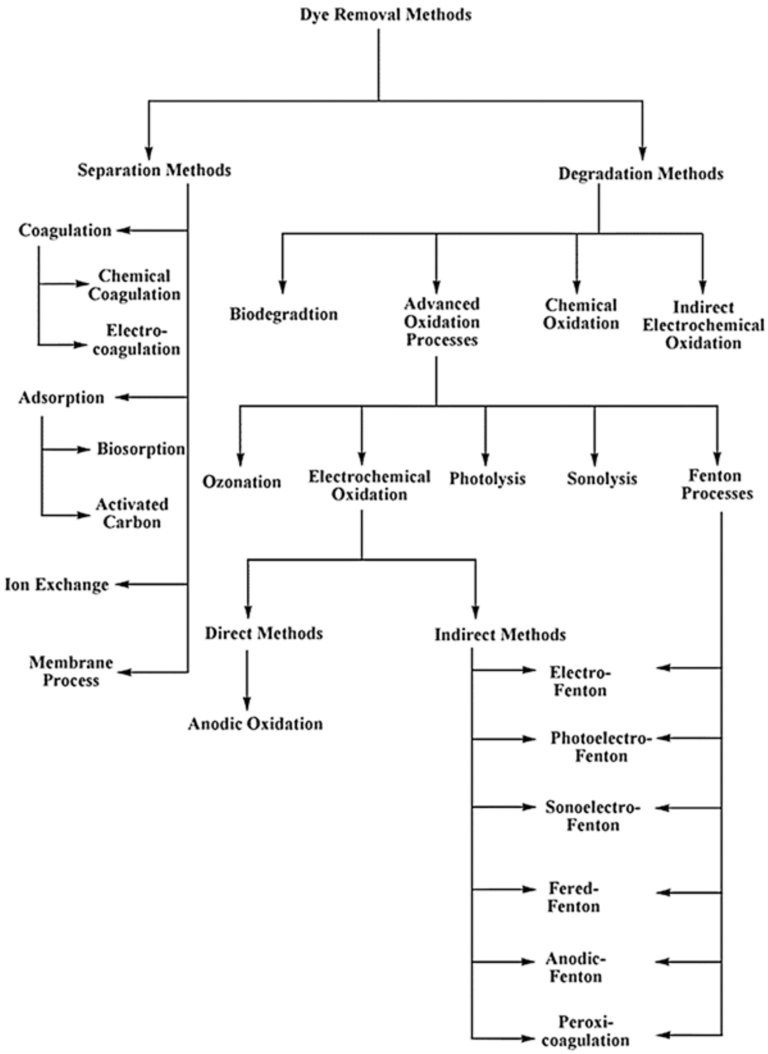

Fig. 11.1 Treatment process of dyes in textile wastewater

With the more quantity of complex material possessing the maximum amount of color, a high concentration of organic changes the features of dyes. With the presence of high BOD/COD, colours and salts, the wastewater dyes of cotton release hazardous pollutants. The coloured water leads to the scarcity of light significant for the growth and development of marine organism resulting in environmental imbalance. Colour and toxic substances should not be present to lessen the cost of the treatment process of river water for consumption purpose. Hence, various treatment processes are formulated and implemented before discharging wastewater into the water bodies in a precise manner which is given in Fig. 11.1.

For the treatment of textile wastewater, different physico-chemical approaches are used, namely, flocculation, chemical precipitation and ion-exchange method (Alqadami et al. 2016). But such approaches are unfavourable as they include expensive costing and even generate secondary waste. In comparison with different techniques, adsorption is the most applicable and even possesses less pollutant. Currently, more interest is generated towards the study relative to absorbents with low-cost materials, namely, tree bark, alum sludge and so on (Clave et al. 2004). The most often applied are the activated carbon, kaolin and silicon polymers. Each adsorbent signifies for selective adsorption of the dye particles. But among all, the activated carbon is considered as the best material. The activated carbon (AC) can remove COD up to 91.15%, and the chroma was reduced up to 92.17% within the reactor meeting the target of the standard wastewater level, and it can even be used again in the form of washing. Since the AC is selective to the adsorbed dye, it is capable enough to remove water-soluble dyes, namely, azo dyes, reactive dyes and basic dyes. But it is unable to absorb the insoluble dyes and the suspended solids present in the dyes. Since the AC possesses high regeneration cost, it is not used directly in original dyeing of textile. Therefore, it is used in low concentration. Ionic liquids (ILs) gathered a lot of attention in the field of engineering and modern chemistry in the industrial application. Lemus et al. (2012) reported that structural characteristics and chemical surface of AC can be modified to adsorb different structures of IL. This property has viability for adsorption of IL according to thermodynamics. Farooq et al. (2012) investigated about the adsorption of hydrophilic IL through AC which stated that both thermodynamics and kinetics of IL adsorption were dependent on AC adsorbent.

11.2 Types of Textile

Sources of textile material are mainly of four types:

- Animal (wool, silk)
- Plant (cotton, jute)
- Mineral (glass fibre, asbestos)
- Synthetic (polyester, nylon)

The first three types of sources are natural, and the fourth source made by the use of petroleum, i.e. artificially. A textile's better property or grade depends on several factors, such as the type of raw material used for making yarn, smoothness of yarn or fabrics, density, etc. (El-Molla and Schneider 2006).

11.3 Location of Textile Industries in India

In India, textile industry is another way to generate vast employment among people both skilled and unskilled, which stands as the second largest industry after agriculture. As per analysis, 2,500 weaving factories and 4,135 finishing factories of textile were present in 2010.

In India, cotton industries are situated in Kanpur, Kolkata, Ahmadabad, Rajkot, Indore, Surat, Vadodara, Nagpur, Mumbai, Solapur, Chennai, Coimbatore and Madurai.

Silk industries are situated in Srinagar, Anantnag, Jammu, Murshidabad, Kolkata, Gokak, Bengaluru, Mysore, Chennai, Coimbatore and Madurai.

Wool industries are situated in Srinagar, Amritsar, Ludhiana, Panipat, Kanpur, Allahabad, Shahjanwan, Mirzapur, Jamnagar, Amalner, Jalgaon, and Bengaluru.

Jute industries are situated in Kanpur, Gorakhpur, Shahjanwan, Katihar, Rajgarh, Darbhanga, Guntur, Vishakhapatnam and Cuttack (Sharma 1949).

11.4 Textile Wastewater

Water treatment is a major problem in the industries (Arfin and Rangari 2018; Arfin et al. 2016). According to standard quality, purifying industrial wastewater must be required before reuse for different purposes; we required some advanced techniques for purification, and these techniques should be efficient and cheap. This treatment required some additional cost for recycling as a product. It can be proved economically more feasible if it takes the low cost of intake water and low discharge cost. Textile industries consume 200 L water per kg of fabrics on an average per day. According to the observation of the World Bank, after finishing and dyeing processes, textile industries produce 17–20 % industrial wastewater.

Textile industries utilize about 80 % of the total amount of the product of 1,30,000 tonnes of dye, in India, because of the high demand of polyester and cotton, and globally these wastewater dyes show a negative impact on photosynthesis process in plant and also on aquatic life due to less penetration power of sunlight. Sometimes these wastewater dyes may be lethal for certain marine life due to the presence of metal and harmful chemicals. And sometimes the particles which are suspended in wastewater may cause blockage into the gills of fishes, and it may lead to death. They also reduce the capability power of algae to make their food. This type of contamination can be detected through municipal wastewater during treatment, for example, ultraviolet decontamination.

Heterocyclic and aromatic dyes are utilized in industries at present. The complex structure of the dye is generally creating difficulty in the process of degradation of

Table 11.1 Textile industrial standards in water pollution

S. No.	Parameters	Standards
1	pH	6.9
2	BOD	30 ppm
3	COD	250 ppm
4	TDS	2000 ppm
5	Sulphide	2 ppm
6	Chloride	500 ppm
7	Calcium	75 ppm
8	Magnesium	50 ppm

dyes. The manufacturing, mineralization and toxicity of dyes in textile industries are major challenges for the environment, so we can say that understanding wastewater treatment from a textile is ecologically noteworthy (Holkar et al. 2016). The textile industries' standard parameters are given in Table 11.1. Wastewater characterization of various textiles are given in Table 11.2 (Bisschops and Spanjers 2003).

11.5 Activated Carbon

Activated carbon (AC) is highly porous, complex and carbonaceous in structure and absorptive; carbon atom contributes in its structural composition. Activated carbon comprises pores which form a network of channels (Waghmare et al. 2015a, b; Waghmare and Arfin 2015). These channels are created inside rigid disordered layers present between atoms of carbon. Pores network linked with the help of chemical bonds. Uneven stack arrangement creates pores due to crevices, perforation, cleft, etc. created between layers of a carbon atom. The high porosity of activated carbon provides about 500 m^2 of surface area per gram of activated carbon; this is determined with the help of adsorption of nitrogen gas.

Various raw materials used in the manufacturing of activated carbon are:

- Coconut shell
- Hard and soft wood
- Peat
- Olive pits
- Lignite coal
- Bituminous coal

The mechanism used in the manufacturing of activated carbon is chemical activation or activation by steam which is at high temperature available from various raw materials. Commercially available forms of this activated carbon are:

(a) Granular activated carbon
(b) Powder activated carbon
(c) Pelleted activated carbon

Table 11.2 Values of wastewater characterization of different textiles

Parameters	Processes	Wool	Cotton	Synthetic	Not Specified
COD	Desizing	–	950–20000	–	10000–12000
	Scouring	5000–90000	8000	–	
	Bleaching	–	288–13500	–	–
	Dyeing	7920	1115–4585	620	–
	Printing	–	–	1515	
					785–49170
BODs	Desizing	–	–	–	200–5200
	Scouring	2270–60000	100–2900	500–2800	–
	Bleaching	400	90–1700	–	–
	Dyeing	400–2000	970–1460	530	–
	Printing	–	–	590	600–1800
Colour (AMDI)	Desizing	–	64–1900	–	–
	Scouring	2000	694	–	–
	Bleaching	–	153	–	–
	Dyeing	2225	1450–4750	1750	–
	Printing	–	–	–	1450
Total solid	Desizing	–	–	–	7600–42900
	Scouring	28900–49300	–	–	–
	Bleaching	910	2300–14400	–	–
	Dyeing	–	–	–	<50000
	Printing	–	–	150–250	–
Total suspended solid	Desizing	–	18–800	–	400–4000
	Scouring	1000–26200	184–17400	600–3300	–
	Bleaching	900	130–25000	–	–
	Dyeing	–	120–190	140	–
	Printing	–	–	–	125–9500
Total dissolved solids	Desizing	–	530–6900	–	–
	Scouring	–	–	–	–
	Bleaching	–	4760–19500	–	–
	Dyeing	–	–	–	55
	Printing	–	–	–	–
Carbon (DOC)	Desizing	–	250–2750	–	–
	Scouring	5800	–	–	–
	Bleaching	–	320	–	–
	Dyeing	–	–	–	–
	Printing	–	–	–	–
Total Kjeldahl nitrogen	Desizing	–	70	–	–
	Scouring	–	–	–	–
	Bleaching	–	40	–	–
	Dyeing	–	–	–	–
	Printing	–	–	164	30–1765

(continued)

Table 11.2 (continued)

Parameters	Processes	Wool	Cotton	Synthetic	Not Specified
NH_4N^-	Desizing	–	9–19	–	–
	Scouring	604	–	–	–
	Bleaching	–	8–19	–	–
	Printing	–	-	129	20–370
Total P	Desizing	–	4–10	–	–
	Bleaching	–	6–60	–	–
	Printing	–	–	21	–
PO_4	Scouring	89.3	–	–	–
Sulphide	Scouring	0.2	–	–	–
	Dyeing	–	325–900	–	–
Sulphate Cl^-	Bleaching	–	–	–	90–100
	Dyeing	–	1750–26500	–	26000
Oil and grease	Scouring	–	580–5000	–	–
Cr^{2-}	Scouring	–	5-0	–	–
pH	Desizing	–	8.8–9.2	–	6–8
	Scouring	7.6–10.4	7.2–13	8–10	–
	Bleaching	6	6.5–13.5	–	–
	Dyeing	4.6–5	9.2–10.1	11.7	–
	Printing	–	–	–	5–8.5
Turbidity	Desizing	–	–	–	930
Waste usage (fabric/kg)	Desizing	–	–	–	12.5–35
	Scouring	4–77.5	2.5–43	17–67	–
	Bleaching	–	30–50	–	–
	Dyeing	40–150	38–143	38–143	–
	Printing	250–520	–	–	20–300

11.5.1 Granular Activated Carbon

Due to the large particle size of granulated AC in comparison with that of powdered AC, thus granulated AC's external surface is small. In processes where adsorbate's diffusion is a primary requirement, granulated AC would be important. Thus, they are preferred in case of adsorption of gases due to their high diffusion rate.

Various applications of GAC involve water treatment, separating components and deodorization.

11.5.2 Powdered Activated Carbon

The composition of PAC involves crushed particles of carbon. Of this 95–100 % will pass through a mesh sieve of a particular designation. GAC is retained on mesh sieve of size 0.297mm. ASTM classified PAC as a particle with size of 0.177mm. In

Table 11.3 Various sources of activated carbon with applications in pollutant removal

S. No.	Source of activated carbon	Activated with	Pollutants removed	References
1.	Sugarcane bagasse	$ZnCl_2$	Basic dye	Fabon et al. (2013)
2.	Bituminous coal	Phosphoric acid	Remazol dye	Teng et al. (1998)
3.	Rice husk	Microwave activated	Dibenzothiophenes	Kumagai et al. (2009)
4.	Coconut husk	Microwave activated	Cyanosine	Gupta et al. (2010)
5.	Nutshell	Microwave-assisted KOH activation	Alkali metal compounds	Foo and Hameed (2011)
6.	Lemongrass	Microwave-assisted activation	Methylene blue	Singh and Tesheing (2014)
7.	Sawdust	Steam pressure	Direct dye	Malik (2004)
8.	Coal	Microwaved	Methylene blue and iodine	Xiao et al. (2015)
9.	Cocoa shells	Microwave activated	Dyes	Kadirvelu et al. (2003)
10.	Grape peel	Microwave-supported activation	Methylene blue	Ma et al. (2018)
11.	Cassava peel	Microwave activated	Dye	Rajeshwarisivaraj et al. (2001)

dedicated vessel, PAC is not used. PAC is directly added to process units; these units include clarifiers, gravity filters, mix basins, etc. (Li et al. 2014).

11.5.3 *Pelletized Activated Carbon*

Pellets are AC compacted into shaped cylinders and have a wide assortment of employments removing contaminants such as mercury. GC C-40 is an example of virgin activated carbon. It is derived from the types of bituminous coal and converts into pelletized form. It shows high surface area and activity.

The source of activated carbon and its application are listed in Table 11.3.

11.6 Ionic Liquids

Ionic liquids (ILs) are ionic species made up of an inorganic anion and organic cation having a melting point less than 100 °C. Figure 11.2 shows the list of few cations and anions of ILs. The constituent of IL varies independently possessing linear alkyl chain and moieties to be functionalized as highly branched, cyclic and aromatic one. It also has a large amount of structure variability. The low melting point of IL is because of the large size of anion and cation and least symmetry

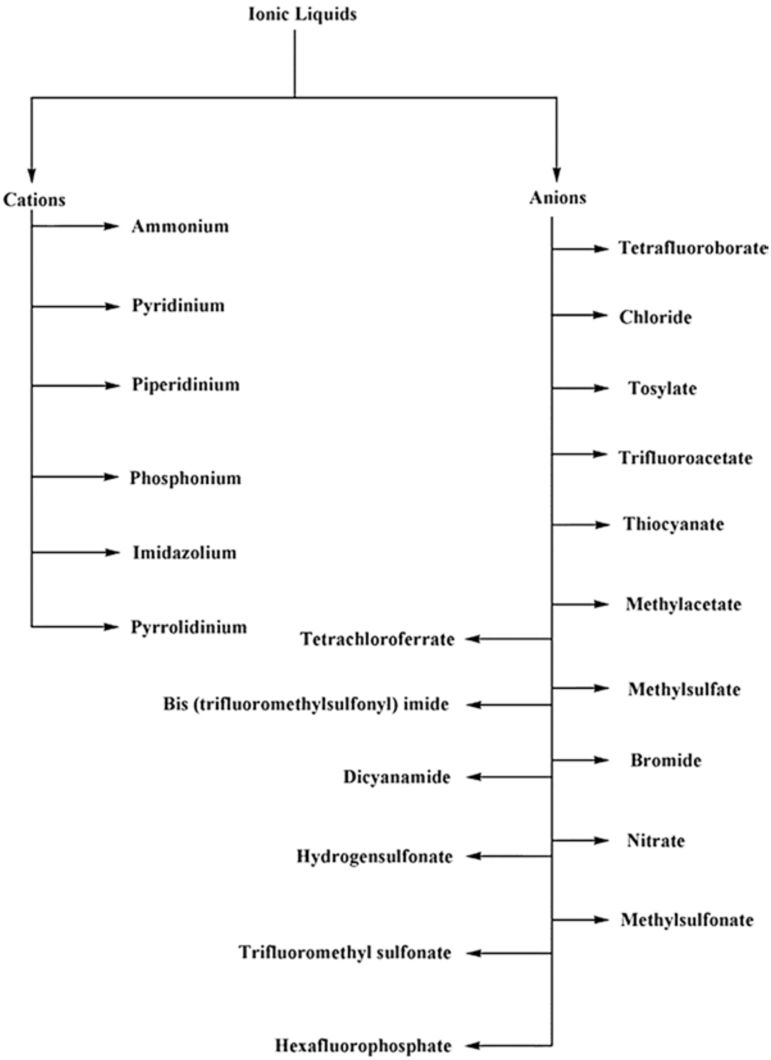

Fig. 11.2 Classic ionic modules of ILs

(Naushad et al. 2012). IL is emerging as a new class of synthesized mixture. It possesses various distinctive physical and chemical properties. Traditional solvents which lead to various environmental damages like ozone depletion, photochemical smog, global warming, etc. are replaced by environment-friendly IL. They are utilized in diverse spheres of industries, synthesizing units which utilize it as a solvent; used as a separating unit at the pilot level of lab work, it assisted in developing various materials which are useful in removing various pollutants that are otherwise

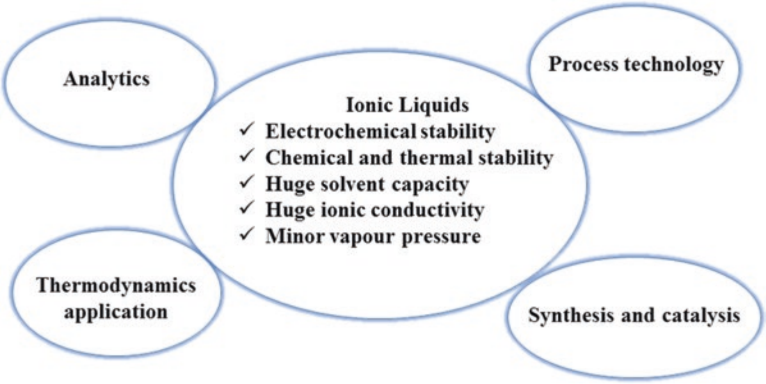

Fig. 11.3 Sketch diagram of ILs and its uses

hard to be removed by conventional methods. To cope up with the increasing demand of IL, it is requisite to study its properties in detail so that IL with desirable properties and composition could be developed further to assist in further industrial processes and material development. Along with desirable properties like electrochemical, ecological, spectrometric, etc., it is necessary for IL to be non-toxic and environmentally friendly when produced at a large scale (Rogers and Seddon 2003).

As the important objective of the current book chapter is related to the research on IL–AC system, the focus is put on the analysis of interaction among the IL and AC. The thermodynamic study of IL adsorption on AC processing various nature, texture of pores generates information about their application in treatment of aqueous effluents with IL. The anion and cation attains the spectrum of IL. The adsorption emphasises the relation between the physical and chemical nature and the adsorption capacity.

Paul Walden reported about the physical characterization of ethylammonium nitrate for the synthesis of first IL in 1914 (Sugden and Wilkins 1929). It could not gather the interest of the research due to various drawbacks. But in the recent year, it is attracted to the field of IL and considered as significant one. After two decades the first patent on IL was published (Graenacher 1934). In the main patent, content was regarding organic salt possessing the ability to solve a problem related to cellulose and change in reactivity. This published patent could not even gather the interest in the scientific fields.

Hurley and Wier synthesized chloroaluminate with IL to generate interest for electrochemistry in comparison with organic and inorganic chemistry in 1948. However, this publication did not generate any noteworthy interest in the scientific community (Hurley and Wier 1951).

In the current scenario, the industrial and commercial application is very astonishing in terms of variety and quantity that arises from industry and academics which is shown in Fig. 11.3.

11.6.1 ILs' Behaviour Towards

ILs are categorized as the green solvents where some of the IL possess thermal and chemical stability and even highly soluble in water. IL may be risky for the environment because of its toxic effects and biodegradable nature. Its synthesis and application in the industry may lead to the formation of waste stream with large amount of ILs in the effluents (Petkovic et al. 2011). Such effluents can also be problematic due to the demand of suitable solution. Hence, to decrease the pollutants of ILs, the efficient strategy is required to remove ILs from aqueous streams.

11.6.2 IL-Based Materials

The IL-based materials bring forward the two types of advanced material mainly based on IL and AC known as supported IL and AC. But according to the application aspect, the use of IL possesses various limitations in mass transfer ratio owing to various physical features, namely, viscosity and high density. And such negative features have led to the innovation of a novel advanced material based on the concept of IL combined with solid support. The combination of IL with solid support is appreciable and favourable to further application. The IL–AC and its application in dye are listed in Table 11.4.

Poole and Poole (2010) have suggested that IL has been proved to be a favourable green solvent applied for chemical processes in reducing the waste in the solvent form by decreasing the dangerous vapours, and it has also been regarded as an eco-friendly material. Welon (1999) have also reported that they possess the property of high solvation. They hold negligible vapour pressure and reduce contamination from the environment by the process of evaporation and are regarded as

Table 11.4 Various IL–AC with applications in dye removal

S. No.	IL–AC	Pollutants removed	References
1.	MimGO sponge	DR 80	Zambare et al. (2017)
2.	Ionic liquid–crafted zeolite	Methyl orange	Xing et al. (2016)
3.	PDVB-IL	Orange II	Gao et al. (2013)
4.	IL@Fe3O4	Reactive black 5	Poursaberi and Hassanisadi (2013)
5.	SAILBO	Malachite green	Elhamifar et al. (2016)
6.	Mt–BMIM	Anionic dye	Belbel et al. (2018)
7.	ILNS	Congo red and reactive blue	Lawal et al. (2017)
8.	Fe_2O_3–cellulose–ionic liquid	Congo red	Beyki et al. (2016)
9.	TCPIL/$CuFe_2O_4$/BNONS	Methylene blue	Arumugam et al. (2018)

significant predictable organic solvents. Leclercq and Schmitzer (2009) suggested that it is an effective replacement for predictable organic surfactants due to its specificity, yielding and high rate.

Lawal and Moodley (2015, 2016) reported about the amaranth dye removal by using the montmorillonite modified with the IL. The material modified is a mixture of macroporous and mesoporous substance generally hydrophobic possessing large pore for trapping the contaminants. The removal percentage reached the maximum of more than 90 % at 2 pH. The Langmuir isotherm best described the adsorption behaviour with a capacity of 263.2 mg/g and the kinetic was described by pseudo-second order. At different concentration, the column experiment employing the Thomas model observed adsorption capacities to be 393.64, 580.89 and 603.60 mg/g. The outcome made it clear that ionic liquid modified montmorillonite served to be the best option for the adsorption technique of the dye from the wastewater of the textile industry.

Lawal and Moodley (2016) performed the adsorption studies for determining the efficiency of IL modified by kaolin. Kaolin modified with IL was put on characterization where adsorption studies were carried out by making use of column and batch processes to remove acid red and phenanthrene. The column models showed that it fitted well for Thomas and Yoon-Nelson isotherm, and the value of R^2 was near to the unit level for both the solutes. The Freundlich and Langmuir isotherms were responsible for describing phenanthrene adsorption showing the capacity of 263 mg/g along with the π–π interactions to be mean sorption. Hence, ILs are applied as a modifier of the adsorption to remove acid red and phenanthrene.

Yan et al. (2015) investigated the use of activated carbon modified with IL for removing methylene blue. The functional group content of the AC surface altered due to modification technique. The absorbance of AC and MAC was used to evaluate the modification. The adsorption process was described by adsorption kinetic models and fitted well with pseudo-second order.

11.6.3 Adsorption Mechanism

Figure 11.4 clarifies about the adsorption mechanism of DR80 on the surface of mimGO sponge. When we go through the structure of DR80, it is basically a dye with a large number of azo linkages along with many anionic sulfonic acid ions and an aromatic ring. The mimGO sponge is hierarchical possessing cationic imidazolium ionic liquid having amide linkages along with hydroxyl functionalities. The presence of π–π interaction among the phenyl ring available in DR80 and mimGO surface also illustrates the adsorption process. Since the hydrogen bond and the π–π interaction are formed in the unmodified GO, there is the unavailability of electrostatic interaction in between the sulfonic acid group of DR80 and nitrogen group of mimGO. Such absence infers that there are low absorption rate and low adsorption capacity as well.

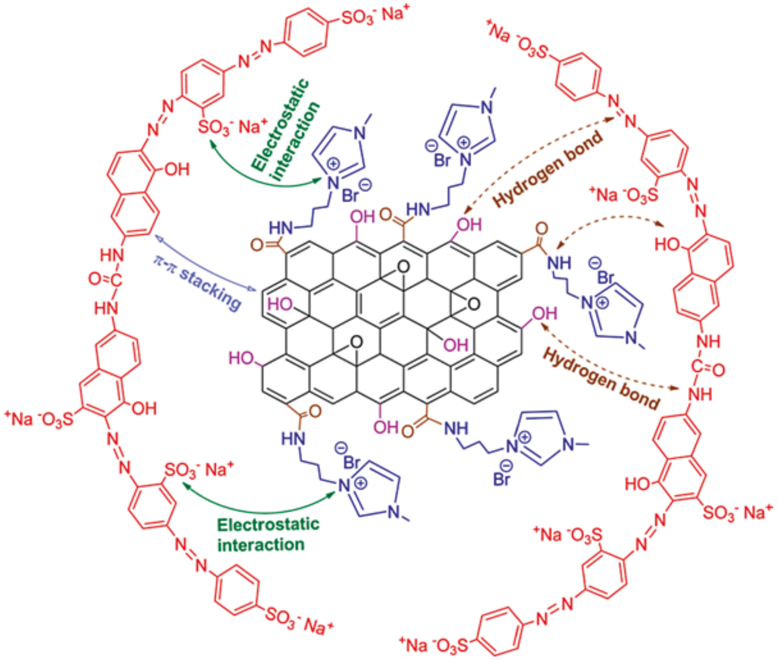

Fig. 11.4 Adsorption mechanism of DR80 on the mimGO sponge. (Reprinted with permission from (Zambare et al. 2017) ©ACS)

11.6.4 Characterization

The scanning electron microscopy (SEM) was performed to exhibit the size of particle and morphology of the surface of SAILBO as shown in Fig. 11.5. Figure 11.5 (a) shows the order of particle in uniform worm-like morphology, and Fig. 11.5 (b) demonstrates about the diverse morphology to compare it with the availability of SAILBO. The result made it clear that adsorption of MG molecule can be either with or without the SAILBO.

The single nanosheet within the composite is shown in Fig. 11.6 (a) and (b). The image of high-resolution transmission electron microscopy (HRTEM) showed that BNONS has sheets which are multilayered with the outer diameter in between 20 nm and 2.5 nm. But it is observed that the HRTEM image is not specific as there is a large electron concentration, and ILs interrupt during the focusing process on the microscope. It is later found that the diameter of the sheet increases between 20 nm and 50 nm just after the modification of IL. It states that there is IL coating on the BNONS surfaces.

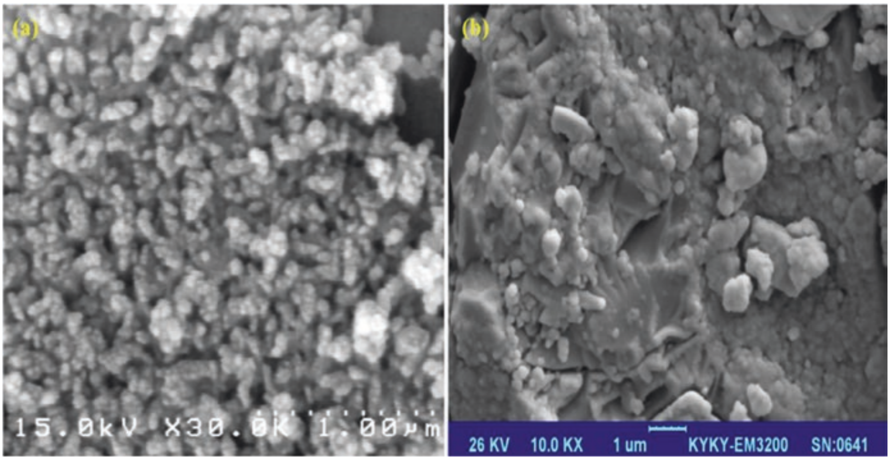

Fig. 11.5 SEM image SAILBO (**a**) before and (**b**) after the adsorption of MG. (Reprinted with permission from (Elhamifar et al. 2016) ©Elsevier)

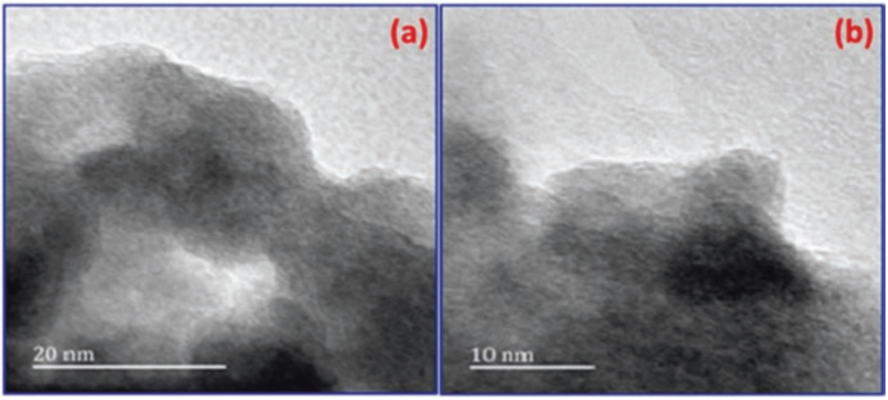

Fig. 11.6 HRTEM images of TCPIL/$CuFe_2O_4$/BNONS nanomaterial at (**a**) 20 nm and (**b**) 10 nm. (Reprinted with permission from (Arumugam et al. 2018) ©Elsevier)

11.7 Conclusion and Future Perspectives

The population increase and unstable rise in the industrialization are giving a serious threat to the safe drinking water on a worldwide level (Arfin and Rafiuddin 2009, 2011; Arfin and Yadav 2012; Arfin et al. 2011, 2012). Therefore, to avoid the scarcity of water, wastewaters from the textile industry can be used as an alternative, but they require proper treatment and purification before using for different purposes which can be a challenging task. Various methods are used for such treatment where innovative technology-oriented process along with conventional process has proved to be the best option. For wastewater treatment, such ionic liquid modified activated carbon is adopted and shows favourable results in the adsorption of dyes and micropollutant.

It has been found that the water industries are advancing the development techniques and providing a cost-efficient system to develop the source of wastewater treatment. Therefore, such advancement in large scale ionic liquid modified activated carbon have proved the way for successful use.

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Chapter 12
Adsorption of Pharmaceutical Pollutants Using Lignocellulosic Materials

Atul Sharma and Saif Ali Chaudhry

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Abstract Water contamination through drug disposal is a prominent problem as it has harsh consequences on food chains. Over 100,000 tonnes of pharmaceutical products are consumed globally every year, and during their manufacture, use and disposal, active pharmaceutical ingredients (APIs) as well as other chemical ingredients are released into the environment. Dry plant matter is called lignocellulosic biomass which is easily available in abundance on the Earth's surface and is composed of carbohydrate polymers (hemicellulose, cellulose) and aromatic polymer (lignin). These polymeric carbohydrates contain different sugar monomers bounded tightly to lignin. Recently, great attention has been paid to remove pharmaceutical pollutants for which various treatment methods are known including both advanced (e.g. membrane, microfiltration, ozonation) and conventional (e.g. adsorption, biodegradation, activated sludge) processes. The aim of this chapter is to discuss the removal of pharmaceuticals using adsorption from wastewater using lignocellulosic materials. Adsorption capacity of various adsorbents from various sources have been reviewed for their capacity to remove pharmaceuticals from water. There are numerous adsorbents including most commonly used carbonaceous materials, clays and polymeric and siliceous materials. The adsorption capacity of various lignocel-

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A. Sharma · S. A. Chaudhry (✉)
Environmental Chemistry Research Laboratory, Department of Chemistry,
Jamia Millia Islamia, New Delhi, India

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lulosic materials for pharmaceutical removal from water is discussed in this chapter. The mechanism for adsorption of pharmaceuticals onto lignocellulosic adsorbents is also discussed herein.

Keywords Adsorption capacity · Adsorbents · Water treatment · Pharmaceuticals

12.1 Introduction

Pharmaceuticals are considered, and recently recognized, as major class of environmental pollutants. The presence of pharmaceuticals, either in surface water or groundwater, near to industrial and residential localities, is seriously a great problem (Fig. 12.1 (Licence Number: 4500651074774)). In the year 1960, the USA and Europe marked the first case of the presence of pharmaceuticals and personal care products (PPCPs), and the concerns about their potential risk were raised in 1999 due to the lowering of feminization of fish living downstream of wastewater treatment plants (WWTPs) after the presence of pharmaceuticals in river was found (Kyzas et al. 2015). Hundreds of different pharmaceuticals have been detected in the environment globally. Entry of pharmaceuticals in the environment can take place in a number of ways:

1. Emissions from manufacturers
2. Human consumption and excretion of pharmaceutical products
3. Improper disposal of pharmaceuticals down toilets and sinks

Designing of active ingredients of pharmaceuticals is done in order to stimulate a response in humans and animals, and some are modified so that they remain unchanged during their passage through the body. Unfortunately, its high stability makes it persist outside the body and, as a result, can have therapeutic effects on un-targeted organisms, and it starts accumulating up. Pharmaceuticals that enter the environment can have unexpected harmful effects on wildlife. One of the worst cases of wildlife poisoning by a chemical has been attributed to a pharmaceutical product, diclofenac. This non-steroidal anti-inflammatory drug (NSAID) caused a

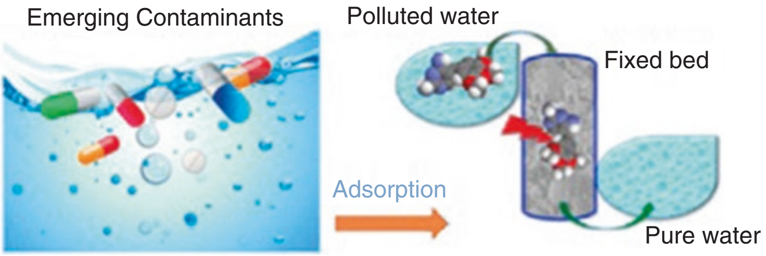

Fig. 12.1 Pictorial representation of contamination of water and its remediation by adsorption technique. (Reprinted with permission from M.J. Ahmed, B.H. Hameed 2018 copyright (2018) Elsevier (Licence Number: 4500651074774))

97% decline in three species of Old World vultures (genus *Gyps*) in Asia, with risk of extinction. Vultures feeding on carcasses of cattle treated with diclofenac suffered acute kidney failure and died within days (https://noharm-europe.org/content/europe/pharmaceutical-pollution-faq). Pharmaceuticals in the environment may also pose a threat to human health (Nabi et al. 2006; Pavithra et al. 2017). Although the concentration of pharmaceuticals may be low, exposure to mixtures of pharmaceuticals with other chemicals could pose a risk to human health. Synergistic effects can intensify the therapeutic properties, and even low concentrations can be dangerous to people for whom a medicine has been given.

There are many remedial methods available for pharmaceutical removal, but one of the advantageous methods with low cost is adsorption (Chaudhry et al. 2016; Siddiqui and Chaudhry 2017a–d). A phenomenon of accumulation of molecules of a substance on the surface of a liquid or solid leading to a higher concentration of those molecules onto the surface is called adsorption (Fig. 12.2) (Chaudhry et al. 2017; Siddiqui et al. 2018a–c). The substance thus adsorbed on the surface is called adsorbate (Siddiqui et al. 2019a–d; Tara et al. 2019), and the substance on which it is adsorbed is called adsorbent (Nilchi et al. 2012; Siddiqui and Chaudhry 2019).

After understanding the pharmaceuticals as pollutant and adsorption phenomenon, now we need to know about the use of adsorption technique in pharmaceutical removal using lignocellulosic material (which is the main aim of this chapter).

12.1.1 *Effect of Parameters on Adsorption*

12.1.1.1 pH Effect

The pH of solution plays a very significant role while dealing with the interactive sorption (Siddiqui and Chaudhry, 2018a, b). Studies revealed that without considering the nature of adsorbent, it is difficult to have a constant adsorption capacity over the entire pH range. So, it becomes very necessary to determine the optimum pH required for a specified adsorption process (Akhtar et al. 2015).

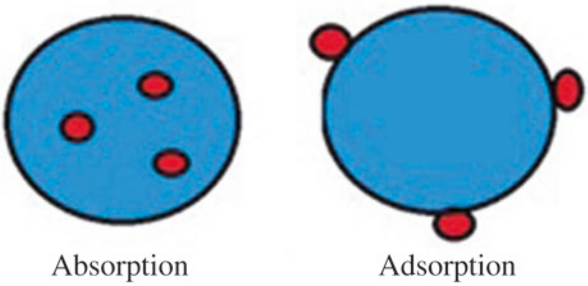

Fig. 12.2 Showing principle of absorption and adsorption

12.1.1.2 Adsorbent Dose

Studies revealed that with the increase in adsorbent dose, there is an increase in percentage removal of pharmaceuticals (Vergili and Barlas 2009; Rossner et al. 2009). This was explained on the basis of increase in availability of vacant sites at higher dosages. Studies reported that saturation value for pharmaceutical adsorption is achieved rarely [96]; therefore, it can be said that further increase in adsorbent dosage is not of measureable significance. Extra dosage leads to removal of extra pharmaceuticals (Akhtar et al. 2015).

12.1.1.3 Concentration of Pharmaceuticals

Initial concentration of pharmaceuticals is a very important factor as adsorption capacity and adsorption rate depend on it. Generally, it was found that adsorption of pharmaceuticals gets boosted by initial concentration. It was also observed that accessibility of pores for adsorbate molecules and interactions at solid–liquid interface increases due to concentration (Akhtar et al. 2015).

12.1.1.4 Temperature

For adsorption process, temperature is an important parameter. It was found that molecular activity at boundary layer interface increases at high temperature, which in turn increases the rate of diffusion of solute molecules. However, literature shows that adsorption behaviour of solute onto a specific adsorbent might also be exothermic in nature (Zawani et al. 2009).

12.2 Lignocellulosic Materials

Three polymers (cellulose, hemicellulose and lignin) constitute lignocellulosic materials (Fig. 12.3). The association of these polymers with each other depends on type, species and even source of the biomass. The relative abundance of cellulose, hemicellulose and lignin are inter alia key factors which determine the optimum energy (Bajpai 2016). The application of these lignocellulosic materials in the removal of pharmaceuticals is majorly studied in this chapter. The composition of monomers of lignocellulosic material is shown in Fig. 12.4. Plant is a major source of lignocellulosic materials (Fig. 12.5).

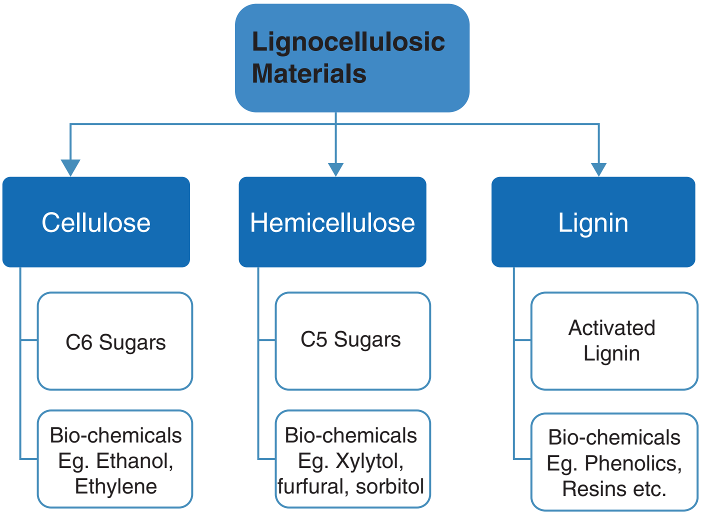

Fig. 12.3 Classification of lignocellulosic material

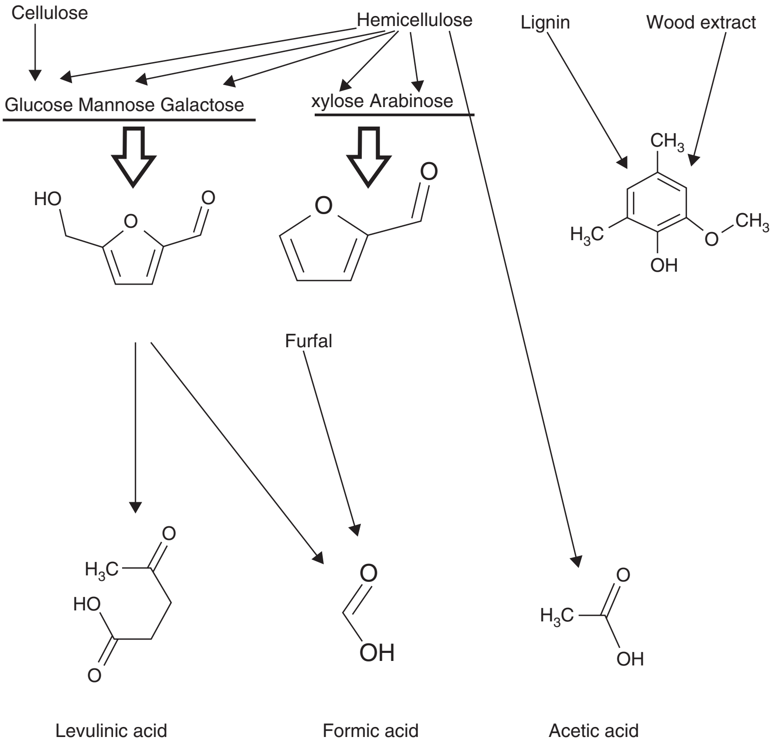

Fig. 12.4 Composition of monomers of lignocellulosic material

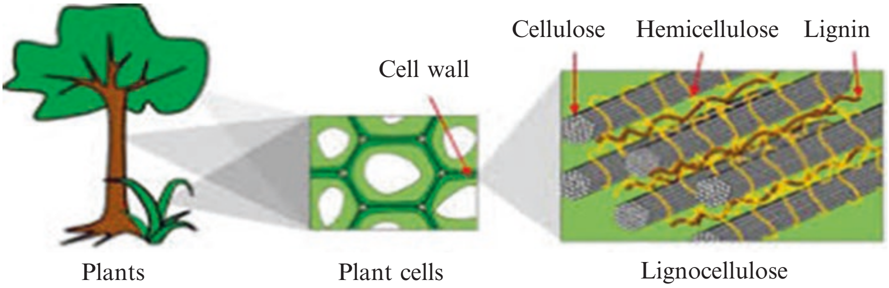

Fig. 12.5 Plants as an important source of lignocellulosic material. (Reprinted with permission from J. Vasco-Correa, X. Ge, Y. Li, copyright (2016) Elsevier (Licence Number: 4500630743190))

12.3 Ways of Reduction in Pollution of Pharmaceuticals in Environment

An important step in pharmaceutical pollution prevention includes reduction of hazardous wastes from source. Reduction in pollution at the source can be possible through the modification in process, replacement of material and good operating practices. The reach of the pharmaceutical industry is increasing day by day, and this makes the industry highly competitive. Each company's confidential policy and high specificity leads to small general discussions of material substitution and process modification. The aim is to target the thinking of manufacturers about their ways of manufacturing processes. One of the best ways to reduce the pharmaceutical pollution is to control it at its source (Fig. 12.6 (Licence Number: 4481750472810)).

There are some industries working successfully in improving efficiency and profit and also in minimizing environmental impacts. Among all, source reduction method is one which serves the primary aim of industries to reduce the wastes. Implementation of source reduction methods is generally quite difficult in pharmaceutical manufacturing units as in other manufacturing sectors. Looking at future aspects, many pharmaceutical companies are finding ways to minimize waste in future production processes by investing in research and development. Using techniques for pollution prevention at the start of a new drug development is more economical, efficient and environmentally favourable.

12.4 Lignocellulosic Materials as Adsorbent for Pharmaceuticals

The adsorption process carried out by biomass is called biosorption (Siddiqui et al. 2017). It contains waste of microbial origin and organic plant materials. These materials have capability to remove the substance dissolved in aqueous medium.

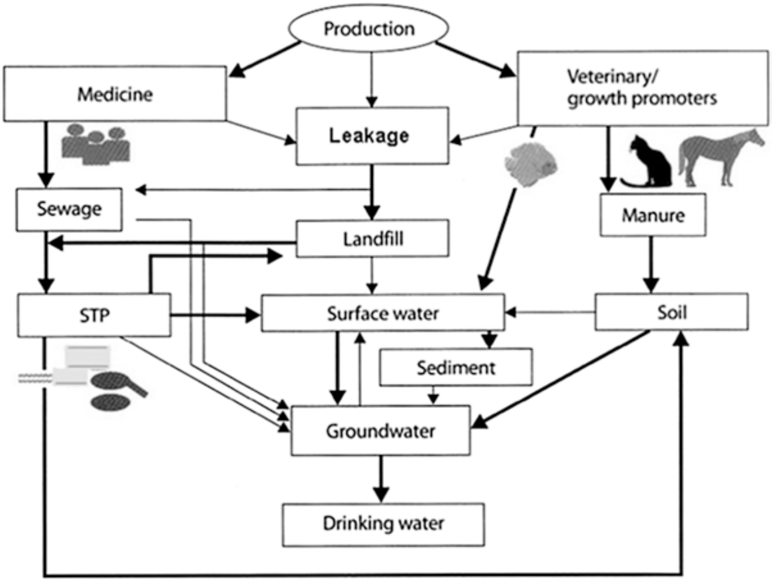

Fig. 12.6 Image showing entry of pharmaceutical into the environment. (Reprinted by permission from Elsevier Zhenxiang He et al. 2016 copyright (2016) Elsevier (Licence Number: 4481750472810))

Lignocellulosic materials serve to be the best material as it involves low cost and has good adsorbent capacity (Fig. 12.7); therefore it can be used for detoxification (Magalhaes and Neves 2006). Biomass is known to be an enhancing agent for adsorption process (Cristavo et al. 2011). For example, sugarcane bagasse and its various polymers like cellulose, hemicellulose and lignin contains functional groups like hydroxyl and/or phenolic, carbonyl groups and amines, and these groups can be modified chemically to form new compounds with various new properties.

Another example is coconut tree which is also an important lignocellulosic material; almost whole coconut tree is used for deriving lignocellulosic material, even the leaves and the fruits. The adsorption capacity of coconut fibre in liquids containing organic contaminants such as gasoline, diesel and lubricants was studied.

Kyzas in the year 2014 said that there is limited research on adsorption of organic compounds such as pesticides, petroleum derivatives and pharmaceuticals using green organic residues, whereas these organic derivatives have been proven to be good adsorbent for removal of dyes and metals.

'Chromatography' is an analytical technique commonly used for separating a mixture of chemical substances into its individual components. There are many types of chromatography, e.g. liquid chromatography, gas chromatography, ion-exchange chromatography and affinity chromatography, but all of these employ the same basic principles; therefore the chromatographic technique serves to be the best method among all the processes known (Boix et al. 2016).

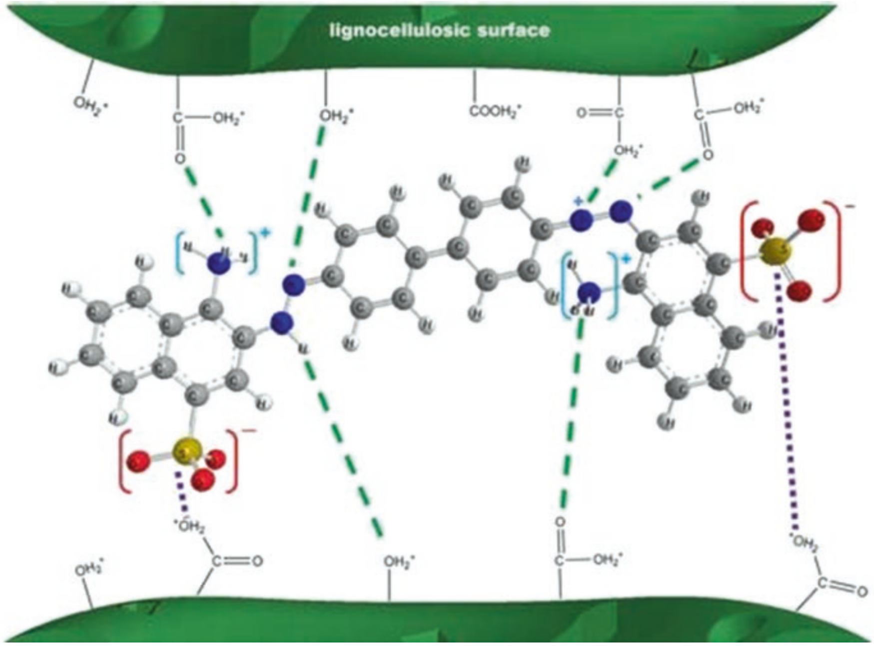

Fig. 12.7 Adsorption phenomenon on the surface of lignocellulose. (Adopted from Yaneva and Georgieva (2012))

Among various tests, one important test of toxicity provides results which give very sensitive values because it not only detects presence or absence of a particular molecule but also provides information about ecotoxicological effects produced after the removal. Among various toxicity tests, the commonly used for the observation of environmental genotoxicity is the *Allium cepa* which is specifically used for wastewater and soil testing (Mazzeo et al. 2015) because it serves as an excellent biomarker of cell mutagenic effects. This test tells about various mutagenic points of the chromosome and also identifies sensitive pollutants, and moreover it has low cost and is easily implementable (Kumari et al. 2011).

Genotoxic effect is estimated in meristematic cells which provide information about genotoxic effects; and changes in the mitotic index indicate cytotoxicity (Mazzeo et al. 2015). The breaks in chromosome and micronuclei in meristematic cell helps to determine the mutagenic potential. **Mazzeo et al**. (2015) tested *Allium cepa* and found that sludge of sewage was mutagenic and genotoxic, even at low concentration. It was found by this test that both pharmaceuticals **thiabendazole** and **griseofulvin** can cause damage to the meristematic cell, which also leads to problems in microtubule like metaphase C, breakage in chromosome of anaphase, multipolar division, bridged anaphase and disorganized anaphase. Therefore, it can be easily said that these tests are important for the collection of ecotoxicological data (Andrioli et al. 2014).

We can also use sugarcane and coconut fibres for the removal of pharmaceuticals from contaminated water, under the hypothesis that the adsorption of pharmaceuticals by these fibres may reduce the toxicity of contaminated water.

12.4.1 Discussion on Adsorption Mechanism of Pharmaceuticals onto Adsorbents

12.4.1.1 Silanol Functional Groups

pH is an important factor in the adsorption of pharmaceuticals such as ketoprofen, carbamazepine, ibuprofen, diclofenac and clofibric acid because it contains various functional groups of silica. The presence of hydroxyl group in –COOH and silanol groups (SiOH) leads to hydrogen bonding, and there is possible interaction between these two groups. The hydrogen bonding can be shown in Fig. 12.8.

These materials possess silanol groups (surface active groups) which explain cationic exchange mechanism and carboxylate group (–COOH) which explains the ligand exchange mechanism. The presence of these groups (silanol and carboxylate groups) leads to a great contribution towards adsorption tendency of adsorbents. Activated carbon can also be replaced by phenolics, carboxyl and lactone functional groups (Putra et al. 2009; Pocostales et al. 2011) that contain acidic and basic groups which have strong influence on the surface charges and enhance the adsorption properties of activated carbon. Adsorption phenomenon, therefore, not only depends on pore structure but also on surface charge because change of surface charges is also an important factor which affects adsorption.

12.4.1.2 Carbonyl Functional Groups

Carbonyl group (C=O) is also a good adsorbing site for binding of pharmaceuticals (Chang et al. 2009). The interaction of cation with the adsorbent can be easily predicted by the shifting of absorption spectrum for C=O towards the higher or lower

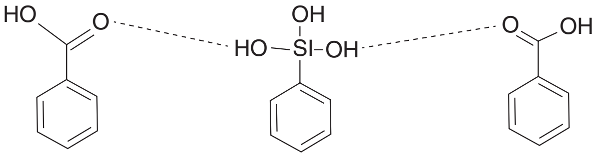

Fig. 12.8 Hydrogen bonding interaction

frequency. For example, adsorption of oxytetracycline onto montmorillonite clay lowers its value from 1685 to 1665 cm^{-1}. For flurbiprofen antibiotic, C=O band is shifted from 1700 to 1708 cm^{-1} after adsorption onto the adsorbent. The binding of C=O group through their charged surface can be explained using cationic exchange mechanism or also through H atom bonded with OH group of water connected to cations on adsorbent surface (Kulshrestha et al. 2004).

The affinity of deprotonated OH group to bind with C=O group is rather greater than the protonated OH group. It was also observed that feldspar or quartz surfaces have deprotonated hydroxyl group attached easily with C=O group of cephapirin antibiotic than to protonated form of hydroxyl group.

12.5 Conclusion and Future Prospects

The environmental impact of pharmaceuticals is not so much clear, and the issue of resolving this problems is quite difficult because science and technology required to fully counter this risk is still in the earliest stages of its development. Human beings are an integral part of this environment. Earlier research has showed that there is inseparable connection between human health and the environmental quality. However, at this moment we need to follow the precautionary principle which signifies that “Any activity which raises threat to human health or the environment, precautionary measures should be taken”.

Numerous proactive measures should be taken to reduce the amount of pharmaceuticals introduced to the environment by various actions of general public. Lignin, being a green material, can serve as a better adsorbent for various harmful pollutants (Fig. 12.9; Order Number: 501453669).

Safety and well-being of patients should not be carried out at the expenses of the safety of communities and the ecosystems. High-quality healthcare and environmental protection are intimately linked. Prevention of pollution establishes a hierarchy in the type of measures that should be taken when dealing with environmental risk. In case of hazardous waste, the following hierarchy needs to be followed:

Fig. 12.9 Pictorial diagram of lignin as adsorbent for various pollutants (Reprinted with permission from Supanchaiyamat et al. 2019 copyright (2019) Elsevier (Order Number: 501453669))

- First: minimization/reduction
- Second: reuse
- Third: recycling
- Last: proper disposition (incineration—waste to energy facilities)

Green pharmacy will be a better alternative for the reduction of pharmaceutical pollutants in the coming future.

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Chapter 13
Titania–Montmorillonite for the Photocatalytic Removal of Contaminants from Water: Adsorb & Shuttle Process

Ridha Djellabi, Mohamed Fouzi Ghorab, Abdelaziz Smara, Claudia Letizia Bianchi, Giuseppina Cerrato, Xu Zhao, and Bo Yang

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R. Djellabi (✉)
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences,
Beijing, People's Republic of China

Department of Environmental Engineering, College of Chemistry and Environmental
Engineering, Shenzhen University, Shenzhen, People's Republic of China

Laboratory of Water Treatment and Valorization of Industrial Wastes, Chemistry Department,
Faculty of Sciences, Badji-Mokhtar University, Annaba, Algeria

M. Fouzi Ghorab · A. Smara
Laboratory of Water Treatment and Valorization of Industrial Wastes, Chemistry Department,
Faculty of Sciences, Badji-Mokhtar University, Annaba, Algeria

C. L. Bianchi
Università degli Studi di Milano, Dip. Chimica and INSTM-UdR Milano, Milan, Italy

G. Cerrato
Università degli Studi di Torino, Dipartimento di Chimica and NIS Interdepartmental
Centre and Consorzio INSTM-UdR, Torino, Italy

X. Zhao
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences,
Beijing, People's Republic of China

B. Yang
Department of Environmental Engineering, College of Chemistry and Environmental
Engineering, Shenzhen University, Shenzhen, People's Republic of China

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Abstract Recently, TiO_2–Montmorillonite-based composites have attracted a great deal of attention as efficient photocatalysts for the degradation/reduction of organic contaminants and heavy metals in waters and wastewaters. It can be claimed that the most popular benefits of using TiO_2–Montmorillonite photocatalysts are an enhancement in the photocatalytic removal of contaminants due to their high adsorption capacity, high photocatalytic activity of nanoscaled TiO_2 deposited on Montmorillonite surface and low costs. Otherwise, the use of naked nanoscaled TiO_2 is not recommended because of its low adsorption ability, fast agglomeration in water and due to the issue of recovery of such small particles from water. Differently from naked TiO_2, the photocatalytic removal of contaminants by TiO_2–Montmorillonite is enhanced through the mechanism so-called Adsorb & Shuttle (A&S) which is based on the use of highly adsorbing domains to increase the quantity of contaminants near TiO_2 photocatalytic sites. Adsorb & Shuttle process can be affected by TiO_2–Montmorillonite characteristics (i.e. TiO_2 loading, surface area, pore size and degree of TiO_2 crystallinity) as well as the type of contaminant. In this chapter, the following points will be highlighted: (i) mechanisms of TiO_2 photocatalysis for the removal of organic contaminants and heavy metals, (ii) recent progress on synthesis of TiO_2–Montmorillonite photocatalysts via different methods and (iii) recent discussions regarding the photocatalytic removal of contaminants by TiO_2–Montmorillonite composites.

Keywords TiO_2–Montmorillonite · Photocatalysis · Adsorb & Shuttle · Water remediation · Organic contaminants · Heavy metals

13.1 Introduction

Due to the dramatic increase in population growth and agricultural and industrialization activities, water demand has increased up to ninefold in the twentieth century (Shenvi et al. 2015). Many countries are expected to face water crisis in the next decades. Thereby, water purification and reuse have become one of the major global concerns in scientific community. Researchers are developing water purification technologies that might be environmentally friendly, economical, and efficient. Among these technologies, the photocatalysis has been considered as one of the most efficient and low-cost processes for water decontamination (Malato et al. 2009; Zheng et al. 2013; Shenvi et al. 2015; Zhang et al. 2018). Titanium dioxide has been extensively in environmental remediation due to its desirable photocatalytic activity, high photostability, non-toxicity, low cost and biocompatibility (Hashimoto et al. 2005; Nakata and Fujishima 2012; Fagan et al. 2016; Waqas et al. 2017). The photocatalysis process is focused on the absorption of UV light by TiO_2 leading to photoexcite the electrons from the valence band to conduction band; therefore, electron/hole pair charges will be formed at the surface of TiO_2. Organic pollutants can be directly degraded by positive holes at the valence band or by the produced hydroxyl radicals via H_2O/positive holes reaction, while the reduction of heavy metals to lower/higher metallic states occurs at the conduction band of TiO_2 by the photogenerated electrons in the presence of hole scavenger molecules (Lee and Park 2013, Lu 2013, Djellabi et al. 2014, Djellabi and Ghorab 2015a, b, Litter 2015, Djellabi et al. 2016a, b, c, Djellabi et al. 2017, Litter 2017, Marinho et al. 2018).

One of the major obstacles facing the implementation of photocatalysis stems from the fact that the photocatalytic removal of pollutants from water depends on adsorption rate of pollutants on the photocatalyst surface. Therefore, it is difficult to photodecompose many hazardous pollutants that hardly adsorb on TiO_2 surface, due to poor affinity of TiO_2 for hydrophobic organic substances. Additionally, industrial wastewaters usually contain several organic and inorganic pollutants which compete for the adsorption sites of the TiO_2 surface, thus inhibiting the efficiency of the process. On the other hand, the photo-oxidation of single organic pollutant can produce many harmful by-products/intermediates that could not be adsorbed on TiO_2 surface for further degradation. It is worth noting that, in practice, the use of nanoscale TiO_2 particles is not recommended due to the issue of recovery of such fine particles from water, and also these nanoscale particles are prone to agglomerate in water limiting the photoactivity. In order to overcome drawbacks of commercial TiO_2, many offers have been made to design new composite photocatalysts via several strategies including metal/non-metal doping, sensitization and coupling of semiconductors. In particular, the combination of TiO_2 nanoparticles with porous adsorbent materials has been proved to be a successful strategy for enhancing the photocatalytic efficiency as reported by several authors (Bhattacharyya et al. 2004; Romero et al. 2006; Zou et al. 2006; Yahiro et al. 2007; Mahalakshmi et al. 2009; Yang et al. 2009; Zhang et al. 2009; Manova et al. 2010; Yu et al. 2012; Vicente et al. 2013; Djellabi et al. 2014; Du and Zheng 2014; Wang et al. 2014; Belver et al. 2015; Yang et al. 2015; Belver et al. 2016; López-Muñoz et al. 2016; Belver et al. 2017; Gebru and Das 2017; Petronella et al. 2017; Srikanth et al. 2017; MiarAlipour et al. 2018). Among these minerals, Montmorillonite has been widely used. Montmorillonite contains layered structure and exhibits very high porosity and high external and internal surface area and large CE capacity which allow the adsorption of organic or metallic pollutants via electrostatic of ion exchange within its interlaminar spaces (Kameshima et al. 2009a; Chen et al. 2012). It is important to point out that the introduction of TiO_2 nanoparticles into layered Montmorillonite enhances the photocatalytic activity due to synergistic effects resulting from the combination of adsorbent and TiO_2. On the other hand, the Montmorillonite can stabilize TiO_2 nanoparticles and increase the concentration of pollutants into the surface of the composite leading to facilitate their degradation/reduction by the photoactive TiO_2 particles. Certain aspects regarding the recent progress on synthesis and application of TiO_2–Montmorillonite for water remediation will be highlighted in the chapter.

13.2 Mechanism of TiO_2 Photocatalysis for Water Treatment

The photonic and mechanistic pathways underlying the phenomenon of TiO_2 photocatalysis for water/air remediation have been extensively investigated and reported (Herrmann 1999; Fujishima et al. 2000; Rauf and Ashraf 2009; Byrne et al. 2017). Photocatalysis is a green strategy that can be employed for environment remediation and energy production using semiconductor photocatalysts under light irradiation. As above-mentioned, titanium dioxide semiconductor (TiO_2) has been largely applied because of its special physical and photonic characteristics. When TiO_2 surface is irradiated by photon energy ($h\boldsymbol{\upsilon}$) of higher than or equal to TiO_2 band gap energy, which is known to be 3.2 eV (anatase) or 3.0 eV (rutile), photo-induced electrons/positive holes changes will be formed at the surface of TiO_2 via the excitation of electrons from the valence band (VB) to conduction band (CB) in femtoseconds. Figure 13.1 illustrates the possible pathways for the production of electron/hole pairs on TiO_2 particle. For TiO_2 case, usually, the photonic excitation requests a light wavelength < 400 nm. A positively charged empty valence band will be produced when the electron moves to the conduction band. Different redox reactions occur at the surface of photoexcited TiO_2 which are responsible for the oxidation and reduction of pollutants and widely reported as follows:

$$\text{Photonic excitation of } TiO_2 : TiO_2 + h\upsilon \rightarrow e^- + h^+ \tag{13.1}$$

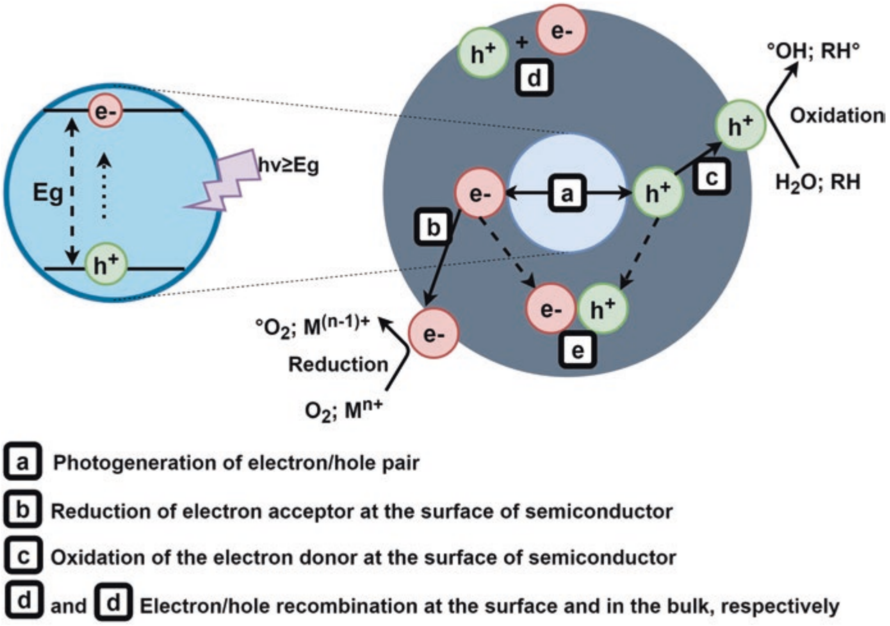


Fig. 13.1 Mechanistic pathways occurring at the photoexcited semiconductor particle

$$\text{Trapping of electrons}: e^-_{CB} \rightarrow e^-_{TR} \tag{13.2}$$

$$\text{Trapping of positive holes}: h^+_{VB} \rightarrow h^+_{TR} \tag{13.3}$$

$$\text{Recombination of charges}: e^-_{TR} + h^+_{VB}\left(h^+_{TR}\right) \rightarrow e^-_{CB} + \text{heat} \tag{13.4}$$

$$\text{Scavenging of electrons}: \left(O_2\right)_{ads} + e^- \rightarrow O_2^{\circ -} \tag{13.5}$$

$$\text{Photoreduction of metallic cations by } e^- : M^{n+} + e^-_{CB} \rightarrow M^{(n-1)+} \tag{13.6}$$

$$\text{Production of hydroxyl radicals}: OH^- + h^+ \rightarrow {}^{\circ}OH \tag{13.7}$$

$$\text{Oxidation of organics by } {}^{\circ}OH : R - H + OH^{\circ} \rightarrow R^{\circ} + H_2O \tag{13.8}$$

$$\text{Oxidation of organics by } h^+ : RH + h^+ \rightarrow R^{+\circ} \rightarrow \text{Intermediate}(s)/\text{Final products} \tag{13.9}$$

$$\text{Protonation of superoxides}: O_2^{\circ -} + {}^{\circ}OH \rightarrow HOO^{\circ} \tag{13.10}$$

$$\text{Co} - \text{scavenging of } e^- : HOO^{\circ} + e^- \rightarrow HO_2^- \tag{13.11}$$

$$\text{Production of } H_2O_2 : HOO^- + H^+ \rightarrow H_2O_2 \tag{13.12}$$

e^-_{TR} and h^+_{TR}in (Eq. 13.4) show the trapping of electrons at the conduction and the holes at the valence band, respectively. It is important to note that the trapping of charges takes place at the surface of the semiconductor, while their recombination does not occur immediately after the photonic excitation (Fujishima et al. 2000). Without the presence of electron scavengers such as oxygen in the medium, the photogenerated electrons can easily recombine with the positive holes accompanying with dissipation of heat energy. Therefore, in order to carry out the photocatalysis action, the presence of electrons acceptor is imperative to avoid the quick electron/hole recombination (enhanced separation of charges ensures an efficient photocatalytic reaction). As shown in Eq. 13.5, the presence of oxygen molecules inhibits the combination of electron/hole pair charges; therefore, the production of superoxides radical $^{\bullet}O_2^-$ takes place. Afterwards, $^{\bullet}O_2^-$ species can be further protonated to produce the hydroperoxyl radical $HOO^{\bullet}$ and then H_2O_2 as indicated in Eqs. 13.10, 13.11 and 13.12. It was reported that $HOO^{\bullet}$ species may also play the role of electrons scavenging at the conduction band which enhances the separation charges. It was deduced that all photocatalytic pathways occur because of the presence of both dissolved oxygen (DO) and water molecules to balance the redox reactions at the surface of the semiconductor. In the absence of water, the highly reactive hydroxyl radicals ($^{\bullet}OH$) can not be produced by the positive holes which limits the oxidation of organic pollutants. Some researchers have reported that the degradation of organics by photocatalytic action does not take place without H_2O

molecules. However, Byrne and Eggins reported that some small organic molecules (e.g., oxalate and formic acid) can be oxidized by photocatalytic system without water (Byrne and Eggins 1998).

While h^+_{TR} has been extensively considered to be a powerful oxidant (+1.0 to +3.5 V against NHE) for the degradation of organic species directly without hydroxyl radicals formation step, this pathway is still quite inconclusive. However, e^-_{TR} is known to be a good reductant (+0.5 to −1.5 V against NHE), which depends on the kind of the semiconductor as well as the reaction condition. Because the photocatalytic oxidation and reduction pathways take place mainly at the surface of the photoexcited semiconductor, the comprehension of the involved steps during the oxidation of organic pollutants is very important in the formulation of kinetic expression. Overall, the degradation of organics usually includes the formation by-products (intermediates) and further mineralized to CO_2 and H_2O as shown in (Eq. 13.13).

$$\text{Organic contaminants} \overset{\text{TiO}_2/h\upsilon}{\rightarrow} \text{Intermediate}(\text{s}) \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{mineral salts} \tag{13.13}$$

Therefore, photocatalysis reaction can be divided into five steps as reported by Fogler and Herrmann (Fogler 2006; Herrmann 1999), as schematically revealed in Fig. 13.2:

1. Transfer of the pollutant species form the solution to the surface of the semiconductor.
2. Pollutant species adsorption into the surface of the photoexcited semiconductor.
3. The photocatalytic reaction takes place for the adsorbed phase at the surface of the photoexcited semiconductor (oxidation of organics and reduction of heavy metals).
4. Desorption of the organics by-products or metallic/metal species from the surface of the semiconductor.
5. Mass transfer of the intermediate(s) from the interface domain to the bulk solution. However, by-products could also be adsorbed on the photocatalyst surface.

Beside the oxidation of organics by photocatalytic action, photocatalytic removal of metal ions from solution by different photocatalysts has attracted much attention recently. The reduction of several metallic cations was investigated and reported in the literature which includes Ag^+, Au^{3+}, Cd^{2+}, Cr^{6+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Pt^{4+}, Rh^{3+}, Tl^+, U^{6+}, Zn^{2+} and As^{3+}(Litter 1999; Kajitvichyanukul et al. 2002; Ruvarac-Bugarčić et al. 2005; Cristante et al. 2006; Kabra et al. 2008; Murruni et al. 2008; Williams et al. 2008; Litter 2009; López-Muñoz et al. 2009; Rodríguez et al. 2010; Lenzi et al. 2011; Singh and Chaudhary 2013; Mahlamvana and Kriek 2014; Mohamed and Salam 2014; Mahlamvana and Kriek 2015; Anggraini et al. 2016; Saien et al. 2016; Guo et al. 2017; Lee et al. 2017; Fontana et al. 2018; Marinho et al. 2018). It is important to note that the photocatalytic ability of a semiconductor such as TiO_2 for the reduction of metal cation can be obtained usually from the correlations of the metal cation redox potentials relative to the TiO_2 conduction band edge, as shown in Fig. 13.3. Many researchers have reported that these potentials can be

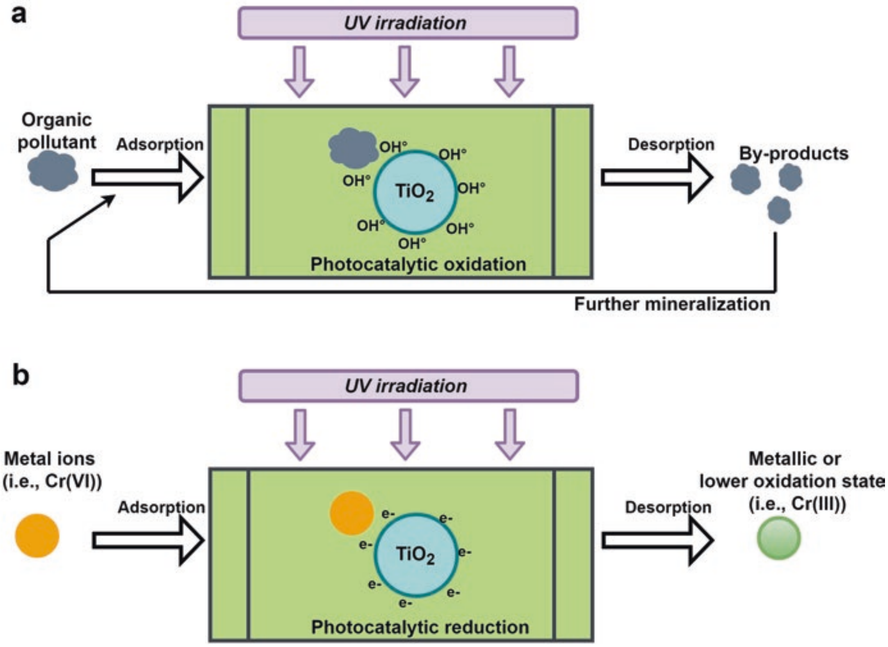
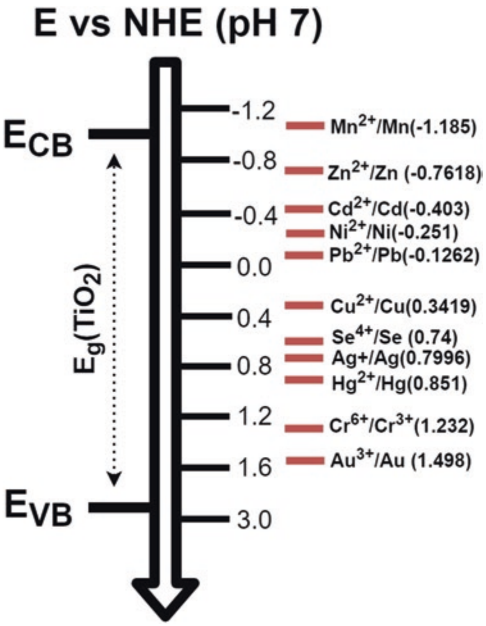


Fig. 13.2 Steps in heterogeneous photocatalytic reaction. (**a**) Oxidation of organic pollutants, (**b**) reduction of metal cations

Fig. 13.3 Positions of CB and VB edges of TiO_2 relative to the standard potentials of several redox couples



shifted by pH or by solution conditions such as the concentration of species and the presence of co-adsorbates. The deposition of produced metal species after the photoreduction reaction on the photocatalyst surface can take place (Djellabi et al. 2016a, b, c). Moreover, in order to ensure an efficient reduction of metal cations, the addition of hole scavenger molecules (sacrificial electron donor) to the solution is very important. The oxidation of organic molecules on the photocatalyst surface allows the separation of electrons for metal cation reduction, as well as inhibits the reoxidation of metal cation. Furthermore, the choice of the hole scavenger molecule (usually a small organic molecule) is a key parameter, since the efficiency of metal cation reduction depends on the balancing oxidation reaction (Tan et al. 2003; Djellabi and Ghorab 2015a, b; Djellabi et al. 2016a, b, c). In addition, several groups have reported that the coordinated ligands to a metal cation such as EDTA can play the role of hole scavenger for the photocatalytic reduction of metal cations.

The mechanisms of metal cations photoreduction by TiO_2 can occur by direct or indirect reduction pathways (Fig. 13.4). The direct reduction takes place via the photogenerated electrons at the CB of the photocatalyst, in which, the conduction band edge of the photocatalyst must be more negative that the $M^{n+}/M^{(n-1)+}$ redox potential. When the metal cation valance charges are higher than 1 (i.e. Cr(VI)), single-electron transfer versus multiple-electron transfer pathways are still not clear. Testa et al. (Testa et al. 2001; Testa et al. 2004) have reported that, via EPR analysis, the single-electron transfer can take place for the photoreduction of Cr(VI) by photocatalysis, in which the reduction of Cr(VI) to Cr(III) passes by the formation of metastable Cr(V). While most researchers envision the direct transfer from CB of TiO_2 to metal cation, some groups (Marinho et al. 2017) have reported that indirect reduction of metal cation could also be possible. They suggested that species, such

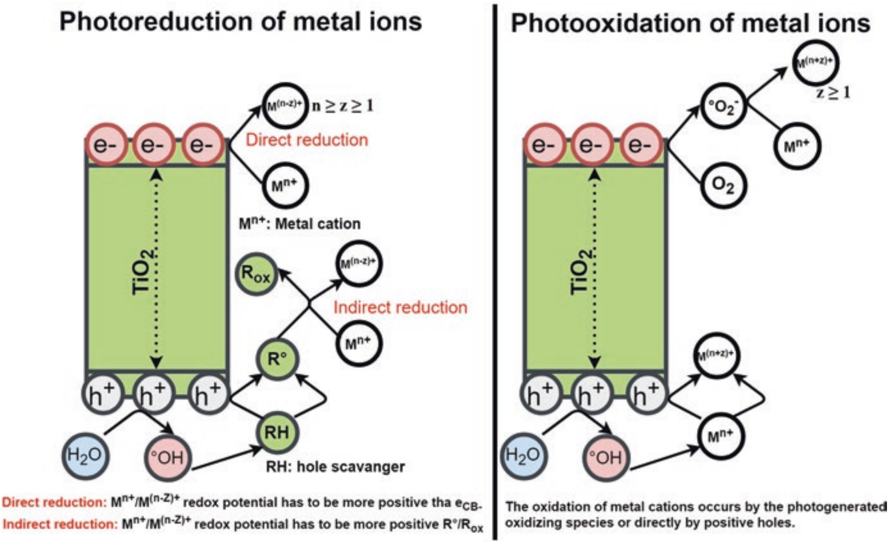


Fig. 13.4 Pathways of photocatalytic reduction and oxidation of metal ions on TiO_2

as $CO_2^{\bullet-}$ ($E_0(CO_2/\ CO_2^{\bullet-}) \approx -2.0$ V), produced through the oxidation of electron donor molecules (hole scavengers) can reduce some metal cations. It is claimed that the indirect electron transfer system occurs independently of the redox potential of the metal ions. Additionally, the oxidation of metal cations, which can reach a higher oxidation state such as As(III) to As(V), can also occurred by the photogenerated oxidizing species or directly by positive holes at the conduction band (Fig. 13.4).

13.3 TiO_2–Montmorillonite-Based Composites

Aluminosilicate clay minerals have been widely used as adsorbents and to immobilize TiO_2 nanoparticles for water and wastewater purification. They are inexpensive, abundantly available and non-toxic and have good sorption properties and ion-exchange potential for pollutants (Özcan et al. 2005). They possess a wide pore size distribution, ranging from micro- (<20 Å) to mesopores (20–500 Å). The high porosity of these minerals is produced from fractures in the particle surfaces, staggered layer edges, whereas spaces are generated by overlapping of stacked layers and interlayer areas (Rutherford et al. 1997). The incorporation of various species and nanoparticles into the interlayer space allows aluminosilicates to be utilized as new functional materials (Yariv 2002). The basic structure of aluminosilicate minerals consists of a tetrahedral sheet of polymerized silica and octahedral sheet of alumina. The alumina octahedra can polymerize in two dimensions by sharing four O atoms, in which two oxygen atoms are left unshared, providing a 2- negative charge. This negative charge is counterbalanced by hydrated cations, e.g. Na^+, Mg^{2+}, Ca^{2+}, etc., which are located in the interlamellar space. Such interlamellar cations are typically exchangeable, while the quantity of exchangeable cations shows the cation-exchange capacity (CEC) of the clay minerals. The Montmorillonites are aluminosilicate minerals which possess 2:1 layer phyllosilicates: two Si tetrahedral sheets are separated by one Al octahedral sheet (T-O-T) (Fig. 13.5). The isomorphic exchanges in the sheets, mostly in octahedral ones for Montmorillonite clays, create deficits of positive electric charges (Volzone et al. 2002). A fundamental

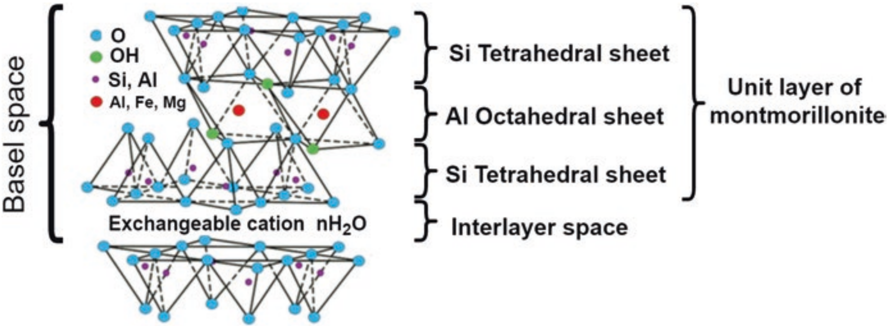


Fig. 13.5 Structure of Montmorillonite

characteristic of Montmorillonite is to absorb water and expand. Therefore, the volume of Montmorillonite increases, and the swelling pressure occurs (Fig. 13.6). The swelling behaviour of Montmorillonite is produced due to two mechanisms defined as crystalline swelling and osmotic swelling. These mechanisms work differently depending on the degree of hydration and the nature of cation in the interlayers.

In recent years, aluminosilicates, especially Montmorillonite, have been widely used as supports of TiO_2 for photocatalytic water treatment. Insertion of TiO_2 into aluminosilicates not only enhances the elimination of organic/inorganic pollutants via simple adsorption due to their high adsorption capabilities but also enhances the overall photocatalytic efficiency by increasing the concentration of species to be oxidized or reduced by active TiO_2 sites. Furthermore, the introduction of TiO_2 particles into the interlays of mineral clay leads to the formation of well-distributed TiO_2 nanoparticles with small size which increases the photocatalytic efficiency (Fig. 13.7). In addition, clay-based photocatalysts are easy to separate from the solution after the photocatalytic treatment. In general, an effective TiO_2 support (i) must be chemically

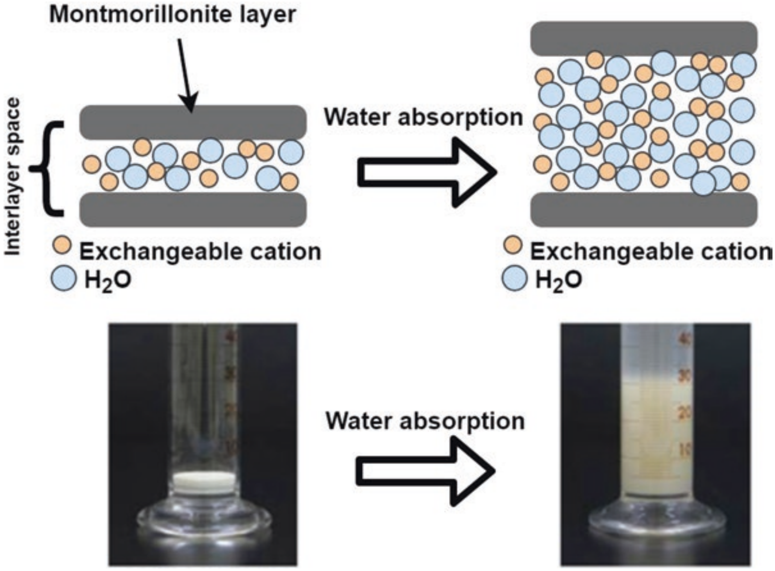


Fig. 13.6 Swelling of Montmorillonite

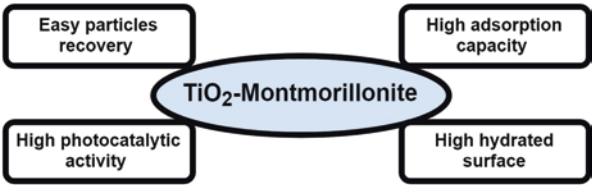


Fig. 13.7 Main advantages of TiO_2–Montmorillonite-based composites compared to TiO_2

inert, (ii) can form bonds with titanium dioxide without diminishing its photoactivity, (iii) has a large surface area and (iv) must be easy to remove after treatment.

13.3.1 Synthesis Methods

For the synthesis of TiO_2-clay/adsorbent-based photocatalysts, there are two ways (Fig. 13.8): (i) insertion/diffusion of TiO_2 nanoparticles powder (commercial or pre-synthesized) into material interlayers by diffusion and (ii) in situ synthesis of TiO_2 deposited into either material interlayers or on the external surface. For the in situ synthesis, the most applied, there are many techniques such as sol-gel, impregnation, chemical vapour deposition and hydrothermal. Various TiO_2–Montmorillonite have been synthesized using different methods for the photocatalytic removal of organics and heavy metals, and a brief comparison is shown in Table 13.1.

13.3.1.1 Sol-gel Method

Sol-gel has been widely used to design of TiO_2/porous support composites. In general, it involves hydrolysis polymerization, followed by drying and thermal treatment steps. The pillaring ways for the synthesis of pillared TiO_2/porous support are usually included in three steps: (i) Ti(VI)-containing compound is hydrolyzed to get $Ti(OH)_4$ sol particles; (ii) intercalation of $Ti(OH)_4$ sol particles into the Montmorillonite interlayers; and (iii) the mixture then is dried and calcined to transform the metal polyoxocations into TiO_2 pillars. However, most of $Ti(OH)_4$ colloidal could not introduce into the interlayer space of Montmorillonite and remained on the external surface, in which TiO_2–Montmorillonite sandwiched structure cannot be obtained. To solve this problem, many research groups have used organic surfactants in order to homogeneously intercalate TiO_2 nanoparticles within the interlayer space of Montmorillonite (Fig. 13.9). These surfactants usually facilitate

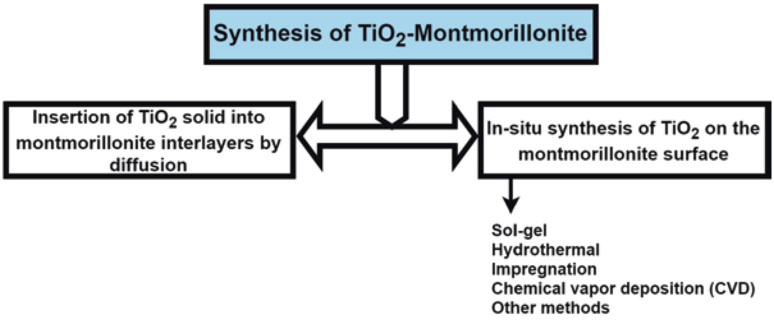


Fig. 13.8 Commonly used techniques for the synthesis of TiO_2–Montmorillonite composites

Table 13.1 TiO_2–Montmorillonite-based composites for the photocatalytic water remediation

Photocatalyst	Synthesis method	Light	Pollutant	References
TiO_2–M	Hydrothermal method with pH switching	UV	Methyl orange	Huo et al. (2018)
TiO_2–M	Solid diffusion	UV	Methylene blue	Liang et al. (2017)
TiO_2–M	Sol-gel	UV	1,4-Dioxane	Kameshima et al. (2009a)
TiO_2–M	Sol-gel	UV	As(V), As(III)	Li et al. (2012)
TiO_2–M	Sol-gel	UV	Hg(II)	Dou et al. (2011a, b)
TiO_2–M	Sol-gel	UV	Methylene blue	Chen et al. (2012)
TiO_2–M	Sol-gel using conventional heating and microwave heating	UV	Solophenyl red 3BL	Damardji et al. (2009a, b)
TiO_2–M	Sol-gel	UV	Di-n-butyl phthalate	Ooka et al. (2003)
			Diethyl phthalate	
			Dimethyl phthalate	
			Bisphenol-A	
M_1–TiO_2–M (M_1: Ag, au, Pd)	Sol-gel	UV, Vis	Chlorobenzene benzaldehyde	Mishra et al. (2018)
TiO_2–M	Sol-gel	UV	Congo red	Dvininov et al. (2009)
TiO_2–M	Sol-gel	UV	Methylene blue	Chen et al. (2014)
TiO_2–M	Electrophoretic deposition	UV	Methylene blue	Rastgar et al. (2013)
TiO_2–M	Intra-gallery templating	UV	Methylene blue	Yang et al. (2013)
TiO_2–M	Sol-gel	UV	Dimethachlor	Belessi et al. (2007)
TiO_2–M	Hydrothermal	UV	Methyl orange rhodamine B	Butman et al. (2018)
TiO_2–M	Impregnation	UV	Methylene blue remazol black	Sahel et al. (2014)
Ag–TiO_2–M				
TiO_2–M	Impregnation	UV	Chlorobenzene methylene blue	Mishra et al. (2017a, b)
TiO_2–M	Impregnation	UV	Methylene blue	Miao et al. (2006)
TiO_2–M	Solvothermal	UV	Methylene blue	Liu et al. (2009)
TiO_2–M	Hydrothermal method/ solid diffusion	UV	Methyl orange	Yuan et al. (2011)
TiO_2–M	Hydrothermal method/ solid diffusion	UV	2,4-Dichlorophenol	Zhang et al. (2015)
TiO_2–M	Sol-gel	UV	2,4-Dichlorophenol	Manova et al. (2010)
TiO_2–M	Sol-gel	UV	Methylene blue, *E. coli*	Fatimah (2012)
TiO_2–M	Hydrothermal method	UV	Pharmaceuticals	Hassani et al. (2017a, b)

(continued)

Table 13.1 (continued)

Photocatalyst	Synthesis method	Light	Pollutant	References
TiO_2–M	Impregnation	UV Solar	Crystal violet, rhodamine B, congo red, methylene blue methyl orange, Cr(VI)	Djellabi et al. (2014), Djellabi et al. (2016a), Djellabi et al. (2016b, c)
TiO_2–M	Impregnation	UV	Methylene blue	Rossetto et al. (2010)
TiO_2–M	Wet grinding in an agate mill	UV-Vis	Phenol	Ménesi et al. (2008)
TiO_2–M	Hydrothermal	UV	Trichloroethylene	Ooka et al. (1999)
Ag–TiO_2–M	Thermal decomposition method	UV	*S. aureus*, *E. coli*	Krishnan and Mahalingam (2017)
Ag–TiO_2–M	Microwave heating/ impregnation	UV, Vis	Chlorobenzene	Mishra et al. (2017a, b)
TiO_2–Fe–M	Impregnation	UV	Toluene	Liang et al. (2016)
TiO_2–Fe_3O_4–M	Sol-gel/coprecipitation under N_2	UV	Methylene blue	Chen et al. (2015)
CdS–M	Hydrothermal method	UV-Vis	Methylene blue rhodamine 6G	Boukhatem et al. (2013)
Fe(III)/ TiO_2–M	TiO_2 pillarization followed by Fe(III) ion exchange	UV	Methylene blue	Fatimah et al. (2015)
N–TiO_2–M	N-doped TiO_2 impregnation with Montmorillonite	Visible	Bisphenol-A	Hsing et al. (2018)
g-C_3N_4/ TiO_2–M	Hydrolysis, dehydroxylation and crystallization	Visible	Organics	CN105107542A
V–TiO_2–M	Sol-gel	UV-Vis	Sulforhodamine B	Chen et al. (2010), Chen et al. (2011)
C–TiO_2–M				
CdS/TiO_2–M	Hydrothermal synthesis	Visible	Methylene blue	Wang et al. (2015)
MgO–TiO_2–Al_2O_3/M	Inflating, intercalation and reassembling method	/	/	Dou et al. (2011a, b)
TiO_2–CeO_2–M	Water-based method	Solar	Parathion methyl	Henych et al. (2017)
SiO_2–TiO_2–M	Hydrothermal method/ solid diffusion	/	/	Kameshima et al. (2009b)
TiO_2–M/ PTP–SDS	In situ chemical oxidative polymerization	UV	Rhodamine 6G	Khalfaoui-Boutoumi et al. (2013)

the access of $Ti(OH)_4$ into the interlayer space of Montmorillonite. Therefore, this method not only improves the dispersion of TiO_2 onto Montmorillonite surface but also leads to improvement the pore size and the surface area by increase of basal space of the Montmorillonite.

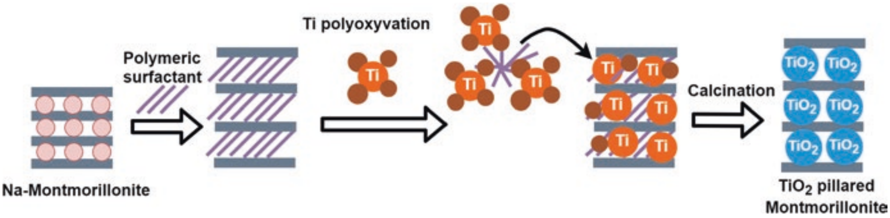


Fig. 13.9 Synthesis of TiO_2–Montmorillonite by sol-gel using organic surfactants

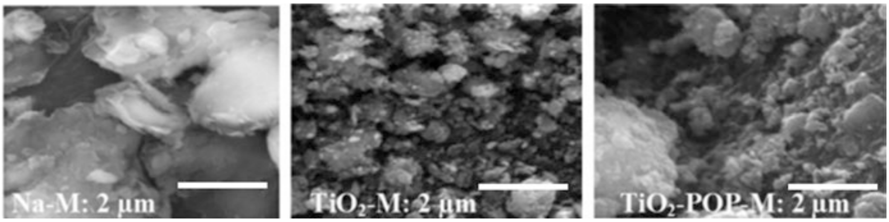


Fig. 13.10 SEM images of Na-Montmorillonite and TiO_2–Montmorillonite synthesized by sol-gel method. (Reproduced with permission: Chen et al. 2012)

Sun et al. (2015) have used cetyltrimethylammonium (CTA^+) surfactant to synthesis TiO_2–Montmorillonite by sol-gel method. They found that the basal space was enlarged from 15.54 Å for the original Ca-Montmorillonite sample to 38.71 Å for CTA^+-Montmorillonite. Tahir et al. (Tahir and Amin 2013) have synthesized TiO_2–Montmorillonite by sol-gel method using isopropanol as a surfactant. They reported that the Montmorillonite controls the crystal growth of TiO_2: the size of TiO_2 nanoparticles decreased from 18.73 (pure TiO_2) to 13.87 nm after adding the Montmorillonite, while the BET surface area and pore volume increased. Chen et al. (2012) have synthesized TiO_2–Montmorillonite by sol-gel method with the high-molecular-weight polymer surfactant POP (polyoxypropylene-backboned di-quaternary salt) as an expand species. They reported that the use of polymer surfactant POP leads to the formation of the delaminated structure and considerably improves the porosity and surface area of the composites. Also, the resulting TiO_2–Montmorillonite exhibited a good thermal stability after calcination at 800 °C. The anatase to rutile phase transformation was not detected even under calcination at 900 °C (SEM images in Fig. 13.10). On the other hand, they reported that the increase of POP amount leads to decrease the size of TiO_2 particles in the composite.

13.3.1.2 Hydrothermal Method

TiO_2–Montmorillonite composites can be also synthesized by hydrothermal method. It is carried out usually under controlled temperature or pressure using steel pressure vessels (autoclaves) with or without Teflon liners. The temperature is frequently elevated above the boiling point of water. Aydin Hassani et al. (2017a, b) have synthesized TiO_2–Montmorillonite using cetyltrimethylammonium bromide (CTAB) as a surfactant, by hydrothermal method (Fig. 13.11). They found that the average crystalline size was 25 nm for pure TiO_2 and 20 nm for TiO_2 in TiO_2–Montmorillonite (SEM images are shown in Fig. 13.12). They suggested that the Montmorillonite can control the crystal growth in TiO_2. However, they obtained that the deposition of TiO_2 did not improve the basal space of the Montmorillonite, which could be explained by the deposition of TiO_2 nanoparticles on the external surface of the Montmorillonite. Zhou et al. (2014) have synthesized CdS–TiO_2–Montmorillonite by hydrothermal method. They reported that the small angle in the XRD spectrum was disappeared after the insertion of CdS–TiO_2 nanoparticles which indicates that the basal space of the Montmorillonite had been blocked by CdS–TiO_2 particles.

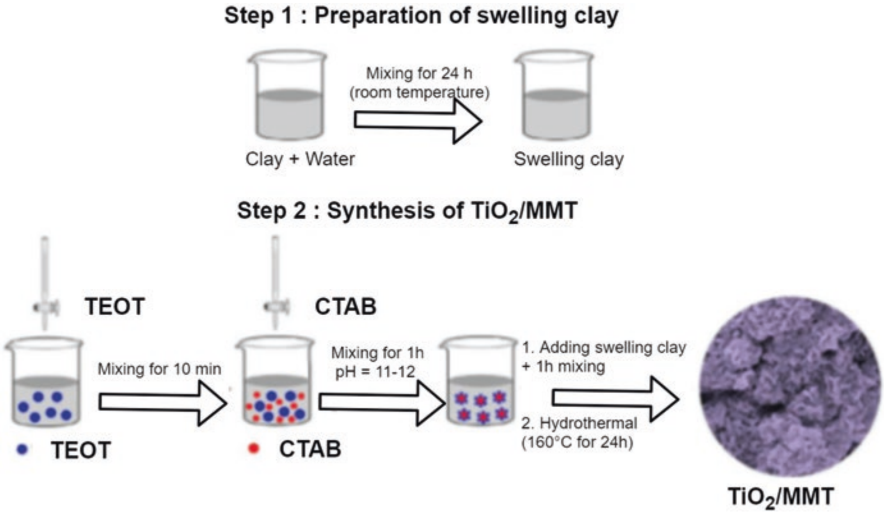


Fig. 13.11 Synthesis of TiO_2–Montmorillonite by hydrothermal method. (Reproduced with permission: Hassani et al. 2017a, b)

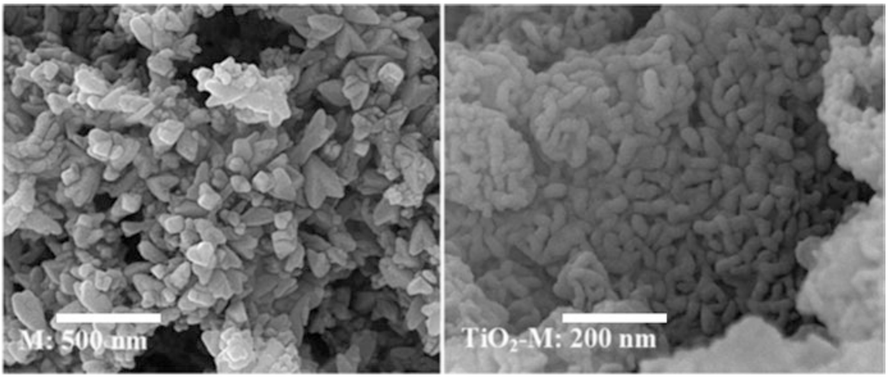


Fig. 13.12 SEM images of Na–Montmorillonite and TiO_2–Montmorrilonite synthesized by hydrothermal method. (Reproduced with permission: Hassani et al. 2017a, b)

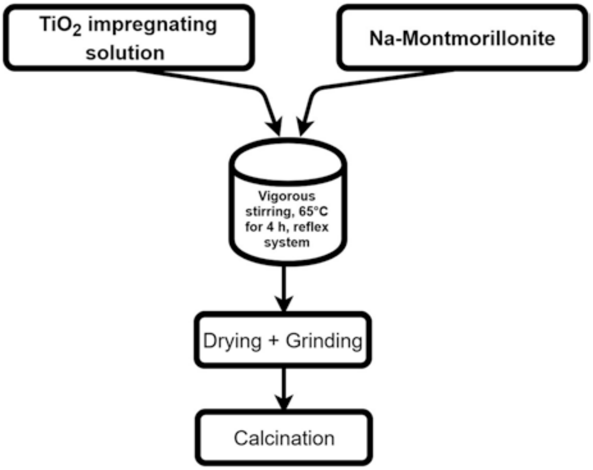


Fig. 13.13 Synthesis of TiO_2–Montmorillonite by impregnation method

13.3.1.3 Impregnation Method

The synthesis of TiO_2–Montmorillonite by impregnation could be simplified as is illustrated in Fig. 13.13, which includes three main steps: (i) contacting the Montmorillonite with the TiO_2 precursor solution, (ii) filtration and drying the composite and (3) calcination of the composite to form TiO_2 crystals.

Djellabi et al. (2016a, b, c) have synthesized TiO_2–Montmorillonite with different weight ratios (g/g) (5, 10, 20 and 30%) by impregnation with $TiCl_4$ (dissolved in C_2H_2) followed by calcination at 350 °C. They reported that the basal spacing of Montmorillonite decreases slightly with TiO_2 loading, while the surface area of all samples was similar to that of Na-Montmorillonite. On the other hand, the average crystallite size of anatase was estimated to be 14–20 nm for all samples (SEM images are shown in Fig. 13.14). Compared to sol-gel method, impregnation method usually does not improve the based space and the surface area since the deposition of TiO_2 nanoparticles takes place mostly on the external surface of the Montmorillonite, while the sandwiched structure could be obtained by sol-gel. Rossetto et al. (2010) have synthesized TiO_2–Montmorillonite samples using different kinds of Montmorillonite by impregnation with $TiCl_4$ (dissolved in cyclohexane), and they found that the surface area of some samples decreased after impregnation of TiO_2.

13.3.1.4 Solid Diffusion

Solid diffusion or power sintering is a simple method to make strong binding force between TiO_2 nanoparticles and porous supports thermal diffusion effect (Wang et al. 2018). Zhang et al. (2015) and Yuan et al. (2011) have synthesized TiO_2–Montmorillonite via the immobilization of pre-dispersed nanoscaled TiO_2 particles

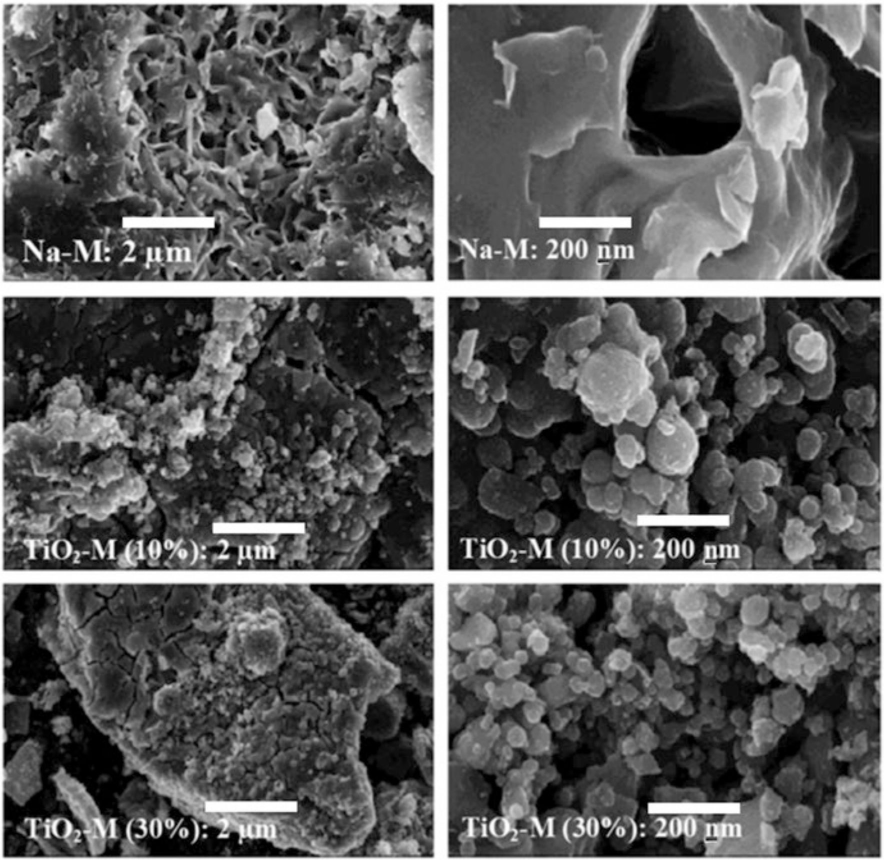


Fig. 13.14 SEM images of Na-Montmorillonite and TiO_2–Montmorillonite synthesized by impregnation method. (Reproduced with permission: Djellabi et al. 2016a, b, c)

onto external surface of Montmorillonite. Firstly, they prepared nanoscaled TiO_2 hydrothermal method with an average size less than 5 nm. Then, they mixed nanoscaled TiO_2-cetyltrimethylammonium bromide (CTAB) solution with swelling-Montmorillonite, and finally, the products were calcined at 500 °C. Yuan et al. (2011) reported that the nanoscaled TiO_2 (with 4.66 nm) could be intercalated into the interlayer of Montmorillonite due to the presence of CTAB (basal spacing increased from 1.26 to 1.87 nm and surface area increased from 28 to 67 m^2/g). Zhang et al. (2015) reported that the increase of CTAB surfactant increases slightly the basal spacing, while, the anatase-to-rutile transformation was observed during calcination at 500 °C. However, it was found that the characteristic reflection for the anatase phase at $2\theta = 25.3°$ was slightly decreased with CTAB increasing (from 0.1 to 0.5 wt.%). They explained that the high CTAB concentrations lead to decreasing numbers and increasing particle size deposited TiO_2 particles into the interlayer. With low CTAB amounts, more TiO_2 pillars can be immobilized in the interlayer

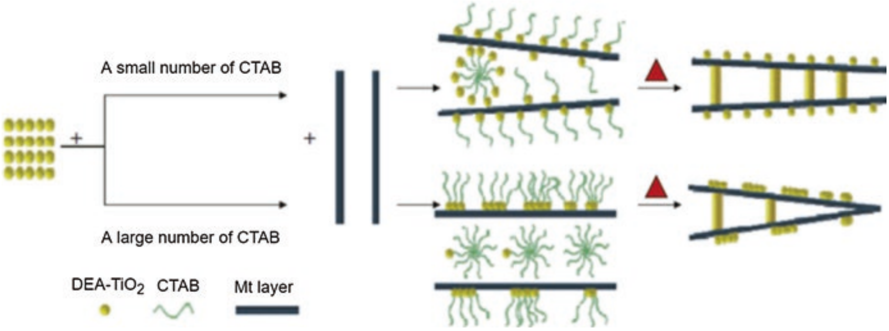


Fig. 13.15 Formation process of TiO_2-CTAB-Montmorillonite according to different CTAB contents. (Reproduced with permission: Zhang et al. 2015)

space, and at the same time, a number of TiO_2 particles with smaller size could be fixed on the external surface of Montmorillonite. On the contrary, with high CTAB concentrations, more CTAB species can block the pores of Montmorillonite, which inhibits the access of TiO_2 colloids to settle into the pores of Montmorillonite (as shown in Fig. 13.15).

Liang et al. (2017) have immobilized pure TiO_2 (P25, Degussa) onto external surface of Montmorillonite using power sintering method proceeding with the following steps: (i) Montmorillonite material and 1 g of P25-TiO_2 were mixed; (ii) a volume of ethanol was added, and the mixture was milled for 30 min and dried at 300 °C for 6 h; and (iii) the obtained solid was grinded. They prepared a series of TiO_2–Montmorillonite of different loads (40%T/M (TiO_2/Montmorillonite), 70%T/M, 80%T/M, 90%T/M, 95%T/M, 98%T/M). The results of TEM morphologies showed that the nano-TiO_2 is loaded successfully onto the Montmorillonite surface. However, when TiO_2 content increases, TiO_2 particles on Montmorillonite surface are prone to agglomeration (Fig. 13.16).

13.3.2 Mechanisms of Photocatalytic Removal of Contaminants by TiO_2–Montmorillonite

The immobilization of nanoscale TiO_2 particles onto the Montmorillonite can assist in improving the contact between the TiO_2 particles and pollutants via the so-called Adsorb & Shuttle *(A&S)* due to its adsorption capability and hydrophobicity property. In general, this concept is based on the use of highly adsorbing domains to increase the amount (concentration) of contaminants near TiO_2 photocatalytic sites and therefore enhance the overall efficiency of the photocatalytic process as shown schematically in Fig. 13.17. Nevertheless, a second mechanism by which the photocatalytic degradation of organic pollutants is obtained through the use of adsorbent support is the diffusion of hydroxyl radicals from TiO_2 from the photocatalytic sites to the adsorbed pollutants on the adsorptive domains, named as "Remote Degradation" (Fig. 13.17).

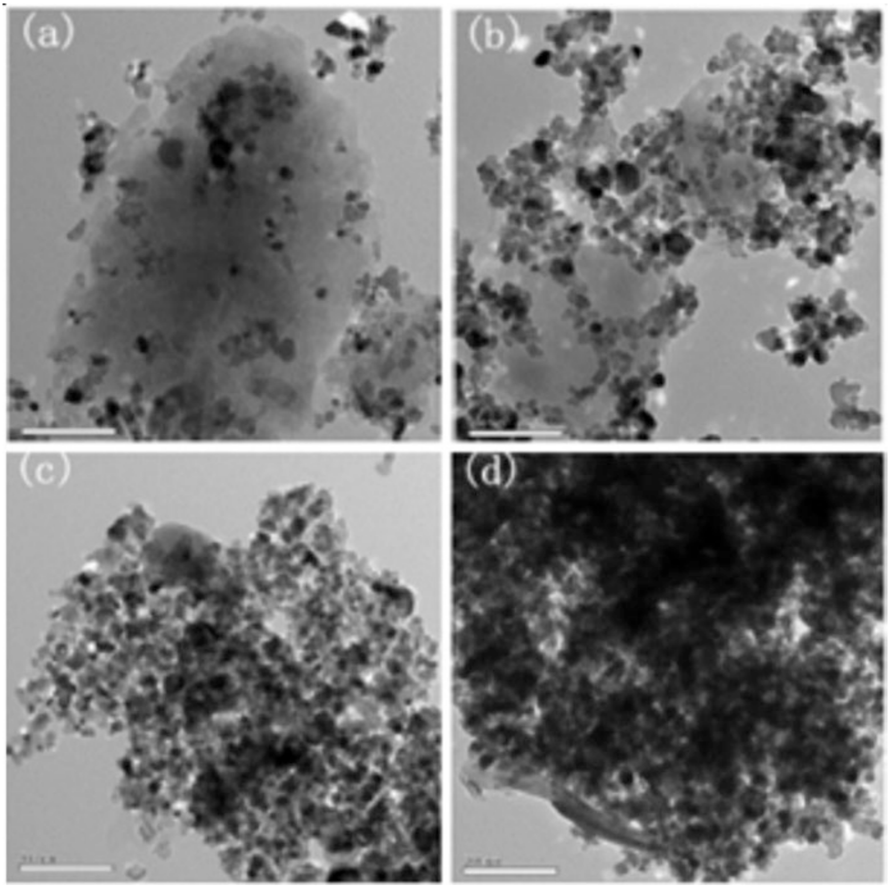


Fig. 13.16 TEM images of TiO_2–Montmorillonite synthesized by solid diffusion process with different load ratios (**a**) 70%T/M, (**b**) 80%T/M, (**c**) 90%T/M, and (**d**) 95%T/M. (Reproduced with permission: Liang et al. 2017)

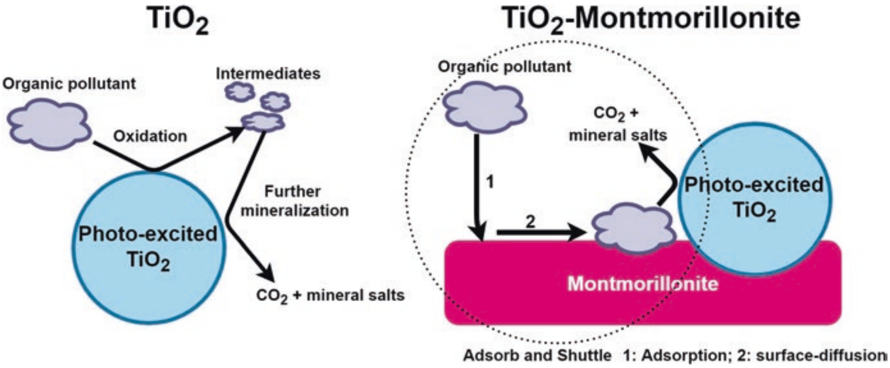


Fig. 13.17 Mechanisms of the photocatalytic removal of pollutants on the surface of TiO_2 and TiO_2–Montmorillonite

Many research studies reported that TiO_2–Montmorillonite composite was more efficient than commercial or synthesized naked TiO_2 (Rossetto et al. 2010; Dou et al. 2011a; Yuan et al. 2011; Chen et al. 2012; Liang et al. 2017; Mishra et al. 2017a, b; Butman et al. 2018). TiO_2–Montmorillonite can combine the adsorption and photocatalytic reaction to efficiently remove contaminants from water (Dvininov et al. 2009; Djellabi et al. 2014). Moreover, TiO_2–Montmorillonite-based composites may retain reaction by-products that are produced during the photocatalytic reaction for further mineralization. Additionally, employing of TiO_2–Montmorillonite overcomes the issue of photocatalyst separation in water purification systems. Because the TiO_2 loading onto Montmorillonite can affect the morphology, surface area, pore size and TiO_2 particle size, it has an important impact on the *Adsorb & Shuttle process*. For higher A&S efficiency, the optimum diffusion distance (distance between the adsorbing domains and TiO_2 sites) should be obtained. Nevertheless, the optimal TiO_2 loading value depends not only on the type of TiO_2–Montmorillonite characteristics but also on the type of pollutant. Higher interaction between the pollutant species and TiO_2–Montmorillonite surface is likely to push the optimum TiO_2 loading towards small values, since high TiO_2 content on Montmorillonite may require a large diffusion distance of pollutant molecules that adsorb strongly on the surface. For the pollutant molecules that adsorb hardly on the surface of TiO_2–Montmorillonite, the reverse is true. It is worth to note that, there is a bottleneck state, in which, the excessive TiO_2 content can block the penetration of light irradiation. At the optimal TiO_2 loading value, the TiO_2–Montmorillonite needs to adsorb contaminants efficiently and then oxidizes/mineralizes them photocatalytically to regenerate the surface for recycling. Djellabi et al. (2016a) have studied the effect of TiO_2 loading onto the Montmorillonite for the photocatalytic removal of Cr(VI) and crystal violet under sunlight. They have synthesized TiO_2–Montmorillonite with different weight ratios (g/g) (5, 10, 20 and 30%), and they reported that the dark adsorption of crystal violet decreases with TiO_2 content increasing, while the Cr(VI) species adsorbs very hardly on TiO_2–Montmorillonite surface (~ 12% for all samples). For the photocatalytic removal under sunlight, they reported that the sample with 10% of TiO_2 loading was the most efficient for crystal violet photodegradation, while for Cr(VI) reduction, the removal rate increases proportionally with TiO_2 loading, and the sample 30% was the most efficient. In a straightforward manner, the fact that the efficiency of TiO_2–Montmorillonite varies from one pollutant to another, using the same sample with 10% of TiO_2 loading, Djellabi et al. (2014) reported that the efficiency of TiO_2–Montmorillonite for the removal of five dyes under UV light was more pronounced for cationic dyes than anionic in the order crystal violet (97.1%) > methylene blue (93.20%) > rhodamine B (79.8%) > methyl orange (36.1%) > congo red (22.6%), which is due to the strong interaction between cationic dyes and the negatively charged TiO_2–Montmorillonite surface.

Dou et al. (2011a) reported that TiO_2–Montmorillonite (with a 22 wt% TiO_2 load) had higher adsorption and photocatalytic activities than synthesized TiO_2 nanoparticles for the removal of Hg(II) from water. They observed that both photocatalysts turned black with Hg(0) nanoparticles under UV illumination. They found that the photo-efficiency of TiO_2–Montmorillonite and TiO_2 nanoparticles decreases after 40 min due to the deposition of Hg metal on the TiO_2 surface, resulting in less reactivity. Li et al. (2012) have used TiO_2–Montmorillonite as an adsorbent to remove As(III) and As(V) from water with or without UV irradiation. They reported that, with UV irradiation of TiO_2–Montmorillonite, the removal rate of As(III) and As(V) increased from 94.58% to 97.71% and from 98.56% to 99.65%, respectively. They suggested that As(III) oxidation to As(V) takes place by TiO_2 particles, followed by fast As(V) adsorption on TiO_2–Montmorillonite surface.

The pore size of TiO_2–Montmorillonite can also affect the A&S process. As explained before, the synthesis conditions including the method, type of surfactants, calcination and TiO_2 loading could affect directly the pore size of TiO_2–Montmorillonite. In general, based on the pore size, materials could be divided into three groups: microporous (< 2 nm), mesoporous (2–50 nm) and macroporous (> 50 nm). Meso- and macroporous adsorbents are suitable for the adsorption/absorption of contaminant molecules with different sizes, which in turn facilitate their photocatalytic decomposition. This was indeed observed by Yuan et al. (2011), who reported that the TiO_2–Montmorillonite sample with higher pore size and pore volume exhibited a higher photocatalytic efficiency for organic molecules. Chen et al. (2012) reported that the photoactivity of TiO_2–Montmorillonite was not a function of TiO_2 loading of the composite photocatalyst, but it depends on the contact between TiO_2–Montmorillonite surface and the dye species. Yang et al. (2013) have synthesized TiO_2–Montmorillonite samples with ordered interlayer mesoporous structure, and they reported that the photocatalytic efficiency for the degradation of methylene blue increases proportionally with increase of pore size.

Butman et al. (2018) have synthesized TiO_2–Montmorillonite samples with high degree of crystallinity (nanocrystals) for degradation of methyl orange and rhodamine B under UV. They reported that the high decolourization rate was due to the higher degree of crystallinity for TiO_2 pillars and higher porosity. On the other hand, they suggested that the anatase and rutile phase ratio can strongly influence the rate of photocatalytic oxidation of dyes. Also, they proposed that the formation of Ti–O–Si cross-links between pillars and silicate layers of Montmorillonite may limit the electron/hole recombination. Therefore, the higher the crystallites of TiO_2, the greater the number of cross-linking bonds can be formed; thus, a higher photocatalytic efficiency is found.

Mishra et al. (2018) have prepared metal-loaded TiO_2–Montmorillonite composites (M = Ag, Au, Pd; 1% by wt.) for the photodegradation of chlorobenzene and benzaldehyde under UV and visible light. It was found that the surface area and pore size increased slightly in the presence of metals. They reported that both the dark adsorption and the photocatalytic degradation of chlorobenzene and benzaldehyde by Metal–TiO_2–Montmorillonite were higher than TiO_2–Montmorillonite under UV and visible irradiations. It is worth to note that, based on their results, TiO_2–Montmorillonite exhibited a photocatalytic activity under visible light. They found that, among the as-synthesized composites, Ag–TiO_2–Montmorillonite shows the highest photocatalytic efficiency for chlorobenzene and benzaldehyde degradation under visible light. They suggested that the high photocatalytic performance of Ag–TiO_2–Montmorillonite may be due to the high excitation lifetime (2.60 ns).

13.4 Conclusions

- Coupling of nanoscale TiO_2 particles with Montmorillonite promotes the photocatalytic performance for the removal of organic pollutants and heavy metals.
- Montmorillonite samples with high specific surfaces areas, high adsorption capacity and high hydrophobicity could be a good choice for the synthesis of effective TiO_2–Montmorillonite.
- Many researchers reported that the Montmorillonite can control the crystal growth and the thermal stability of TiO_2 better than naked TiO_2.
- The use of polymer surfactants during the synthesis of TiO_2–Montmorillonite such as cetyltrimethylammonium (CTA^+) and polyoxypropylene-backboned diquaternary (POP) allows intercalating homogeneously TiO_2 nanoparticles within the interlayer space of Montmorillonite (obtain a sandwich structure) and reduces the agglomeration of TiO_2 particles, and it improves the pore size and the surface area by increasing of basal space of the Montmorillonite. It is worth noting that the concentration of surfactant should be optimized.
- TiO_2 loading in the Montmorillonite can affect significantly the structure of TiO_2–Montmorillonite depending on the synthesis conditions; at high loading, TiO_2 is prone to agglomerate and block the pore of the Montmorillonite.
- The photocatalytic removal of organic pollutants and heavy metals is carried out through the so-called Adsorb & Shuttle (A&S), in which pollutants adsorbed on the adsorbing domains (Montmorillonite) diffuse on the surface to the TiO_2 photocatalytic. The Adsorb & Shuttle process efficiency depends strongly on the TiO_2–Montmorillonite characteristics (TiO_2 loading, pore size, adsorption capacity and TiO_2 particle size) as well as the type of pollutant.
- Unlike naked nanoparticles TiO_2, TiO_2–Montmorillonite is a low-cost and environmentally friendly photocatalyst which prevents the release of TiO_2 nanoparticles to the environment, and it can retain reaction by-products that are produced during the photocatalytic reaction for further mineralization.

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Chapter 14
Jet Fuel from Domestic Wastewater Treatment Using Microalgae: A Review

Joseph K. Bwapwa, Anandraj Akash, and Cristina Trois

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J. K. Bwapwa (✉)
School of Engineering, Howard College, University of Kwazulu-Natal, Durban, South Africa

Faculty of Natural Sciences and Faculty of Engineering, Mangosuthu University of Technology, Durban, South Africa
e-mail: joseph@mut.ac.za; josephkapuku@gmail.com

A. Akash
Faculty of Natural Sciences and Faculty of Engineering, Mangosuthu University of Technology, Durban, South Africa
e-mail: akash@mut.ac.za

C. Trois
School of Engineering, Howard College, University of Kwazulu-Natal, Durban, South Africa
e-mail: troisc@ukzn.ac.za

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Abstract Domestic wastewater can contain numerous toxic substances making it a public health hazard. Recycling wastewater with the possibility of reuse can be considered as a viable option. Various ways of remediation are being used to solve the issue of water pollution. The current review analyses the possibility to use microalgae for wastewater treatment followed by the conversion of biomass into aviation fuel. It is well known that conventional wastewater treatment plants are energy demanding and pollutant removal processes are not always cost-effective. Furthermore, sludge management is another issue that requires a sustainable solution to reduce its environmental footprint. Algae biotechnology can be an option that can be used to overcome these challenges. Microalgae species such as *Nannochloropsis*, *Euglena*, *Oscillatoria*, *Chlamydomonas*, *Scenedesmus*, *Chlorella*, *Nitzschia*, *Navicula* and *Stigeoclonium* have the ability to accumulate contaminants/pollutants, therefore reducing the pollutant/contaminant load from wastewater. Removal efficiency can reach up to more than 90% for organic substances, nitrates, phosphates and heavy metals. Microalgae species supply also oxygen to aerobic microorganisms. This can reduce the costs related to oxygen supply in a conventional plant. Once clean effluent is generated, algae biomass is harvested and used for bio-jet fuel production. The biomass is processed to produce crude bio-oil which has similar physical properties compared to the petrochemical crude oil. Algae bio-oil can be processed via transesterification, thermal cracking or pyrolysis and fractionation including reforming and upgrading processes to produce renewable jet fuel. This fuel is expected to have the same physico-chemical properties compared to conventional jet fuel. It is environmentally friendly due to its low carbon footprint. However, the major challenge with algae-based fuels is the low lipid content for many species and the costly biomass harvesting process.

Keywords Wastewater · Nutrient removal · Microalgae · Bio-jet fuel · Conversion processes · Algae biofuels · Algae biotechnology

14.1 Introduction

14.1.1 Energy Demand and Biofuels

The world demand for energy is increasing every year, and the interest for alternative fuels more especially biofuels including biodiesel, bio-jet fuel, bioethanol and biohydrogen has grown very fast. However, petroleum-derived fuels are still remaining as the leading and sustainable source of energy. According to the International Energy Agency (IEA), an average of 85 million barrels of petroleum is used up worldwide on a daily basis. Also, the demand for primary global energy is growing yearly at the rate of 1.6%. Predictions from various models indicate that the primary and the global demand for energy will become twice greater than currently over the next four decades. In addition, the IEA estimates that there is a strong need to introduce low carbon fuels into the pool of global energy in order to stabilize atmospheric CO_2 levels. As the current focus on the protection of the environment is progressively dominant, with the price volatility for oil being an undeniable truth, many countries are considering the use of renewable energy more especially biofuels as backup plan to any eventual energy crisis that could take place in the near future.

It is well known that many countries are relying on fossil fuels in the transportation sector. Unluckily, fossil-based fuels despite their competitive costs compared to biofuels are considered as the most polluting with high volumes of greenhouse emissions released daily in the atmosphere. These emissions constitute the major cause for global warming and climate change. Hence, the consequences linked to climate change and global warming are immeasurable in today's environmental context. A need for reliable source of energy to generate less carbon is needed in order to remediate to the current environmental challenges. Biofuels generate low carbon emissions below the environmental standards, and they could be considered as an appropriate alternative in the near future despite some of the weaknesses.

They are also expected to be sustainable and have the same level of performance than fossil fuels. In some cases, they are used entirely in engines or are blended with their petroleum counterparts. This last option has presented many advantages economically and technically.

14.1.2 Necessity of Using Biofuels in the Current Context

The global increasing demand for energy is a major challenge today that requires effective solution because various factors such as the level of industrialization, the rapid increase of the population and the lifestyle have an impact on energy consumption. Furthermore, the limited reserves of fossil fuels constitute a cause for concern regarding the availability of energy sources in the near future. A need for innovation to secure a better future for transportation fuels and energy production particularly is very vital. Therefore, newly developed technologies and sustained innovations hold the promise of efficient results through a mixture of energy efficiency and renewable energy such as biofuels (Larkum et al. 2012; Tabatabaei et al. 2015). There is a need for solutions that can defy the existing meaning of energy sources and the way energy should be used or deployed. In recent years wind, solar and hydrogen energy have been developed; these energy forms are not practical in meeting energy and transportation needs due to size, scale and cost application. However, biofuels such as bioethanol, biohydrogen, biodiesel and bio-jet fuel from sources that will not cause inflation of food crisis and reduce environmental problems are currently the most regarded alternatives (Mata et al. 2010). There has been a real progress regarding development stages of biofuels in order to improve their effectiveness and sustainability. Biofuels have moved from first to the fourth generation with different improvement and advancement aspects introduced from one generation to another one.

14.1.3 Different Generations of Biofuels

The first-generation biofuels were generated from food crops by extracting the lipids or oil from seed rape. Thereafter a transesterification reaction was undertaken to produce biodiesel. From biodiesel there is a possibility to produce other biofuels via conversion process such as cracking, decarboxylation, pyrolysis and isomerization. For instance, the production of bioethanol was achieved via fermentation using crops such as wheat or sugar as feedstock. These biofuels have encountered some challenges but the most contentious problem is the threat to the food security. The conflict between food and fuel was rising. First generation of biofuels has caused the diversion of food crops from the global food market towards fuel market causing price increases for the raw materials used to generate biofuels which are the same used in the food market (Naqvi and Yan 2015; Naik et al. 2010; Mohr and Raman 2013; Lee and Lavoie 2013; Dutta et al. 2014).

The second generation of biofuels was initiated with the aim to overcome some limitations encountered from the first-generation biofuels. Non-food crops were chosen to produce biofuels using feedstocks such as wood, food crop wastes or used edible oil and biomass in order to eradicate completely the main the use of food crops. Second generation of biofuels are being cost-competitive compared to existing petroleum-based fuels. It has been shown from life cycle assessment that the net energy gains will be increased. This is another aspect that allows to overcome one of the main limitations from the first generation. Second generation of biofuels use mostly biomass from agriculture residues or non-crop plants such as switchgrass. The use of these biomasses will help to reduce the pressure on the global food supply. Additionally, they require small amount of space and can generate higher biofuel yields when compared to the first-generation feedstocks, and they may be cultivated on a land with a lower quality. However, the current data related to the economics of second-generation biofuels have reported that commercial scales will never be viable until significant are developed. Technological advances will require the investment of time and money in order to use these biofuels. Consequently, second-generation biofuels are not likely to play an important role to supply fuels in the short and medium term, unless specific improvement and ground-breaking technologies are developed (Naik et al. 2010; Schenk et al. 2008; Damartzis and Zabaniotou 2011; Lee and Lavoie 2013; Dutta et al. 2014).

The third generation of biofuels have aimed to improve the production of biomass. In this category, specially engineered organisms or crops with considerable energy content such as microalgae are highly explored. Algae biomass is cultivated at lower costs, and its energy content is very high with the capacity to be renewable in very short periods of time. Therefore, less strain on freshwater resources for algae growth (Dragone et al. 2010; Carere et al. 2008; Lee and Lavoie 2013; Dutta et al. 2014).

The fourth-generation biofuels focused more on production of highly clean source of energy such as biohydrogen from biomass or feedstocks such as microalgae and organic wastes. Also, the aim is not only to produce sustainable energy but to find ways to capture and store carbon dioxide. This carbon dioxide will be used to feed the biomass in order to convert it into sustainable fuel. The sequestration of carbon dioxide is part of the process, and there are many ways to store carbon dioxide. It can also be stored in gas fields or saline aquifers. The carbon capture can become negative than neutral. In this case more carbon is locked than emitted; therefore less carbon emission will be recorded (Demirbas 2009; Dutta et al. 2014; Aro 2016).

14.1.4 Algae Biotechnology and Biofuels

Future prospects involve the third and fourth generation of biofuels which are focusing on the identification of feedstocks with very high lipid content and the use of innovative ways to extract oil and produce low costs, low carbon emission and sustainable fuels. Algae biotechnology is a highly explored option and could be one of the foremost players in the renewable energy market for biofuels such as biodiesel, biohydrogen, bioethanol and bio-jet fuel. Though algae biofuels present few challenges such as high costs for harvesting drying and downstream processes, algae require fewer inputs, it is the fastest-growing biomass and can be grown anywhere, and there is no strain on food products, therefore solving some challenges recorded from the two first fuel generations. The main benefit of using algae-based biofuels compared to other biofuels is that algae do not compete with agricultural or limited resources such as freshwater resources and land. Algae-based fuels are low carbon content fuels. They can contribute in limiting the effects of greenhouse gas (GHG) and recycle CO_2 emissions during biomass cultivation. This is a very important fact because the growth of algae depends not only on nutrients but also on carbon dioxide. Therefore, power plants can reduce sensibly their CO_2 emissions in the atmosphere by supplying CO_2 to algae producers. Consequently, algae processing plants will not only produce fuels but will also reduce the effects of climate change. The main objective for algae biofuel production especially algae-based jet fuel is to get drop-in fuels complying with standards and ready to be commercialized. It is obvious that the demand for bioenergy resources will carry on increasing because of the influence related to the current renewable energy and climate change guidelines and strategies (Wilhelm and Jakob 2011; Scott et al. 2010; Huang et al. 2010). The World Energy Council has indicated that biofuels will reach 30% of the global energy demand by 2050. Therefore, there is a significant potential for biofuels in general and bio-jet fuel in particular to be considered as an alternative to fossil fuels. However, more innovative ways are needed to improve the production processes, to identify the most promising feedstocks that can generate more lipids or to develop methods to stimulate the increase of lipids from the various feedstocks. More emphasis can be put on the third- and fourth-generation biofuels because they are not competing with the food industry and they can generate low carbon fuels. The economics of these fuels need to be improved by using optimized processes and low-cost feedstocks. This chapter is only focusing on biotechnology aspects and conversion processes needed to produce bio-jet fuel from microalgae.

Details on the economics of the conversion processes from microalgae to jet fuel can be undertaken in specific studies.

14.1.5 Rationale of This Review

The rationale behind this review is to show if both treatment of domestic sewage assisted by microalgae can generate biomass and lipid essential for jet fuel production. Two streams can be generated: the treated effluent to be reused for other applications and the crude bio-oil from the biomass to be converted into jet fuel. Many challenges have to be addressed in order to generate a sustainable jet fuel from microalgae.

14.2 Approach to Produce Microalgae Jet Fuel and Problematic of Feasibility

It is important to stress on the fact that the literature on algae-based fuels particularly algae- based jet fuel is very scarce. Although many studies have been undertaken in this specific field, most of the valuable information involving major ground-breaking findings is not in the public domain. Technological improvement is a critical and major step required to produce a competitive algae-based jet fuel being on a market currently dominated by petroleum/conventional jet fuel. The probable approach will be to duplicate and adapt the same technology used to produce conventional jet fuel from crude oil to produce algae-based jet fuel from algae crude bio-oil. This approach will require process modelling and optimization to produce a drop-in jet fuel. The demand for jet fuels is very high and will always increase because of the market dynamic reflected by consumption of jet fuel. This consumption is expressed in volume of jet fuel needed on a daily/monthly/yearly basis by civil and military aviation. The economics of producing algae-based jet fuel is currently still not cost-competitive compared to the economics of producing conventional jet fuel.

Ongoing research seeks to improve technologies to enable the production of algae-based jet fuel to commercial level. Many projects on bio-jet fuel from microalgae are undertaken currently on laboratory and pilot scales, but still they are not yet implemented at commercial scales. Therefore, the challenging concern focuses on developing cost-effective conversion processes and increasing algae lipid content as mentioned earlier.

Globally, energy production is among key factors that are essential to economic and industrial development. However, the production of fossil fuels through traditional petrochemical processes is seen as the major cause of environmental pollution and climate change effects as mentioned earlier. Furthermore, reserves of world fossil fuel resources are very limited and may lead to scarcity in the near future. To reduce dependence on fossil fuels, the production of cost-effective biofuels can be considered as one of the options to be explored. The aviation sector is facing challenges involving cost fluctuations and environmental issues related to the use of fossil fuels. These challenges can have an impact on the viability of many businesses. Algae-based fuels present many advantages that can be beneficial to the aviation industry. However, to get algae-based jet fuel to the level of competing with the current fossil-based jet fuel will require many complex problems and adjustments in terms of cost-effectiveness and sustainability.

14.3 Current Context for Jet Fuel Production and Consumption

Currently, 2% of the global CO_2 emissions is generated by the aviation sector. It is estimated that the global demand in terms of fuel consumption for the aviation industry will carry on in increasing until mid-term of 2030 (Blakey et al. 2010). Consequently, the environmental impact of aviation regarding the GHG emissions is likely to increase. Furthermore, it was reported that an increase in demand will take place in the early 2000s and will be ranging from 3.5% to 5% per passenger km flown (Wickrama 2001; Blakey et al. 2010). Also, ever since the 2009 economic downturn till date, it is suggested that the demand will get back to its previous rate once there is an improvement from the global economic situation (Rosenfeld et al. 2009). The air freight will be subjected to the same trend despite the fact that a decline in demand was recorded due the economic downturn (Nygren et al. 2009; Blakey et al. 2010). Up to 2030, it is predicted that the subsequent increase for jet fuel consumption will be at a low rate, while the passenger demand is on the increase.

This is mainly due to two factors: firstly, increases in fuel efficiency for the aircraft fleet which will be estimated at 1.2% reduction per annum (Nygren et al. 2009; Blakey et al. 2010) and secondly, through air traffic management optimization. Furthermore, the International Air Transport Association (IATA) has predicted a growth in jet fuel demand ranging from 190 million tons in 2009 to 300–350 million tons by 2030 (Wickrama 2001; Blakey et al. 2010). As a result, a proportional increase of CO_2 emissions will be recorded. It is very important to stress on the fact that environmental sustainability for commercial aviation is not the only concern, the availability of crude oil is another one, the petroleum oil reserves are decreasing and so far, there are no sustainable and commercialized substitutes to compete with fossil fuels. Alternative jet fuels from many resources are being developed, and probably technology will offer new routes or innovation processes to generate sustainable fuels. In this regard, algae-based jet fuel is seen as one of the plausible options to be explored as there is a record of successful attempts regarding its blending with petroleum jet fuel as it is mentioned in the next section.

14.4 Previous Attempts on the Use of Algae-Based Jet Fuel

Some biofuel producers have attempted to produce jet fuel from microalgae, and they have concluded that there could be a potential in using microalgae species to produce aviation fuel. Some of these producers are Sapphire Energy, Heliae, Phycal, Cellana, Solazyme and General Atomics, to name a few. The renewable jet fuel from microalgae produced by these companies has successfully been used as trials in both commercial and military aircrafts. Their blending with conventional jet fuels on 50–50 basis (known as B50) was approved for use in commercial flights by ASTM International. Continental Airlines inaugurated the first-ever commercial test flight in the USA in January 2009.

A Continental Boeing 737 departing from Houston International Airport flew up with a B50 fuel blend made of algae-based jet fuel and conventional jet fuel in one of its two engines. This was part of the biofuel blending plan from Continental Airlines aiming to reduce the impact of fossil jet fuel in the environment. This event was considered as the beginning of a new era regarding the development of alternative jet fuels. In June 2011, the US Navy successfully established a B50 blend made of both microalgae-based jet fuel and conventional jet fuel. This blend was produced by Solazyme, and it was used in a MH-60S Seahawk helicopter. It was an occasion where algae-based jet fuel was used for the first time in a military aircraft. In July 2011, ASTM International announced its certification for blending conventional jet fuel with other biomass-based jet fuels including algae-based jet fuel. The certification was based on 50% blending in volume ratio (B50). This certification allows the use of renewable aviation biofuels from biomass to be used by the aviation industry on a B50 basis only. However, this certification is open door for future studies on various blending options and ratios, the conditions of their improvement and optimization that can also lead to new certification. Therefore, there is a gap to be filled with regard to new alternatives for jet fuel blending. Similarly, a blended jet fuel made of 40% algae jet fuel produced by Solazyme was used to fly United Flight 1403 aircraft from Houston to Chicago in November 2011. This was another US commercial flight using a blend made with algae-based jet fuel. These trials have sufficiently demonstrated there is potential in using microalgae-based jet fuel to reduce dependence on fossil fuel. However, many challenges mentioned early are still yet to be addressed.

14.5 Requirements to Produce Microalgae Biomass for Renewable Jet Fuel

14.5.1 Microalgae Selection

It is important to emphasize on the fact that one of the crucial steps to a successful production of microalgae-based fuel starts with the choice of an appropriate microalgae strain (Brennan and Owende 2010). There are approximately more than 50,000 existing microalgae species, but only 30,000 are characterized, and some are still under study (Mata et al. 2010). This implies that with the amount of existing species, many possibilities could be explored to produce variety of algae-based jet fuel or other algae-based fuels such as biohydrogen, biodiesel and biogasoline. However, it is obvious that several aspects have to be taken into consideration and analysed meticulously in terms of the nature of species, the cultivation mode, the contamination, the lipid content and the possibility to increase it in order to select the most reliable species/strain that has great potential to produce a sustainable jet fuel.

14.5.2 Lipid Content

Microalgae lipid content is one of the key characteristics required for biofuel production (Schenk et al. 2008). The production of crude bio-oil and eventually the jet fuel will mainly depend on the lipid content of the strain or species. When choosing the strain, one has to decide whether to go for the very high lipid content accompanied with low cell productivity or moderate lipid content accompanied with high cell productivity (Mata et al. 2010), as these two characteristics are mutually exclusive in natural strains (Ratledge and Cohen 2008). Generally, it has been reported that microalgae accumulate between 10% and 50% of their dry weight in oil content (Chisti 2007). Oil accumulation higher than 50% is usually associated with cell productivity (Schenk et al. 2008). However, there is also a possibility to increase the lipid content by modifying the genetics of the strain. This can be done by nutrient starvation or the use of enzymes or genetically modified organisms to stimulate oil increase in the cell. The process is completed after cultivation; the biomass will be subjected to conditions that involve physiological modification of cells under starvation conditions. This will therefore stimulate the metabolism of cells and induce an increase of biomass quantity and lipid content. The genetic engineering of strains is generally a successful technique used to increase the strain or species lipid content. However, it is depending on the nature and species type. Each species or strain has its own way of responding to physiological modification involving nutrients starvation or use of enzymes.

14.5.3 Site Selection

Another important step in microalgae cultivation is the choice of an appropriate site. The assessment of a potential site can involve several criteria that have to be inspected and regulated. These criteria are classified into two categories: abiotic and biotic factors (Moheimani 2005). Generally, abiotic factors are related to characteristics such as the quantity and quality of light and water supply, the water salinity, the amount of dissolved oxygen and carbon dioxide, the pH of water, the surrounding climate including temperature (Schenk et al. 2008), the rate of evaporation and precipitation and the availability of nutrients and carbon sources (Moheimani 2005). It is well known that both light and temperature play a major role when it comes to microalgae productivity (Mata et al. 2010). However, the light used for cultivation should be at the optimum value to ensure effective growth of cells. Strong and intense light can lead to photoinhibition causing harm to effective photosynthesis required for better microalgae growth and biomass production (Moheimani 2005; Ginzburg 1993). Therefore, it is vital to match the algae strain with an appropriate environment in which sunlight can sufficiently be provided to help grow the strain effectively (Ginzburg 1993). Each strain or species has its own optimum growth temperature which allows it to reach its maximum growth rate. However, the optimal growth temperature for microalgae growth ranges between 20 and 30 °C (Chisti 2007). It is assumed that a decline in temperature can be tolerated by most microalgae strains, while an increase by only 2–4 °C from the optimal microalgae temperature can lead to a destruction of the culture (Chisti 2007; Mata et al. 2010). Creating sufficient space for microalgae cultivation in a conducive environment or site is very important to allow a sustainable biomass production. The topography and geology of the land will also require a careful consideration, the land slope must be less than 10%, and soil depth must be minimal to allow the construction of cost-effective large cultivation systems (Schenk et al. 2008).

The resources required for microalgae growth including carbon and water must be easily accessible; they should be situated within the vicinity of the chosen site in order to reduce the costs related to transport and handling. Various strains/species can grow in different aquatic media such as freshwater, seawater as well as brackish water (Ratledge and Cohen 2008); consequently, the stress on freshwater can be reduced. The use of saline water depends on the selected site; this can be situated next to coasts or nearby saline groundwater. On the other hand, the biotic factors include the presence of parasites and predators competing with microalgae growth and preventing nutrients to be assimilated by cells (Moheimani 2005; Mata et al. 2010).

14.5.4 Microalgae Nutrients

Nutrients are essential to generate significant amounts of biomass from microalgae culture. The nutrients needed are mainly inorganic compounds such as CO_2, phosphorus and nitrogen (Chisti 2006). The provision of these elements for microalgae growth is generally inexpensive when using wastewater treatment ponds (Powell et al. 2009). Large portion of hydrocarbons (90%) formed through microalgae photosynthesis are made from carbon, whereas the other 10% is made of hydrogen (Ginzburg 1993). Moreover, 50% of the dry biomass weight is attributed to carbon content (Patil et al. 2008). The carbon source needed by microalgae through biological uptake can come either from the 0.03% of carbon dioxide available in the atmosphere or from the flue gases generated by heavy industries and fossil fuel power plants. This CO_2 can be fed to the culture to contribute to cell growth and increase biomass production rate. Also, lipid content is increased because of the increase in carbon chains (Brennan and Owende 2010).

However, in case there is a dependence only on atmospheric CO_2 as carbon source, the productivity of microalgae cells will be lower and not suitable for fuel production because of low biomass generated during cultivation (Posten and Schaub 2009). Microalgae have a significant uptake capacity for CO_2 compared to many terrestrial crops. This is due to their faster growth and high nutrient absorbance capacity. Microalgae can grow on arid land; however, they cannot replace forests which constitute an important carbon sink (Khan et al. 2009). It is reported that 1 kg of microalgae can absorb approximately 1.83 kg of CO_2 (Chisti 2007; Patil et al. 2008). The efficiency of CO_2 uptake by microalgae ranges between 30% and 99%, depending on the cultivation system used and the rate of culture mixing (Reijnders and Huijbregts 2009). This mechanism of CO_2 uptake allows the recycling of CO_2 (Mata et al. 2010). The CO_2 absorbed by microalgae during growth is re-emitted during microalgae biofuel combustion (Mata et al. 2010).

Another important nutrient is phosphorus, an energy carrier element and an essential constituent for cellular metabolism and regulation contributing to the production of enzymes and phospholipids in microalgae (Moheimani 2005). It represents 1% of microalgae dry biomass weight (Powell et al. 2009). It is a main component of adenosine triphosphate (ATP) needed for the storage and transfer of short-term energy as mentioned before. It is an essential parameter in the microalgae energy metabolism. It is also involved in the synthesis of nucleic acids, lipids and proteins which have an influence on bio-oil output. Inorganic phosphates contribute sustainably to the growth and metabolism of algae cells.

Nitrogen is also one of the most important nutrients for microalgae cells; it is the main component of chlorophyll. It is also a major producer of amino acids, the building blocks of proteins contributing to the increase of cell lipid content. It is a macro element that plays an important role in the synthesis of protein and genetic material. It is known as an essential element which contributes significantly to the growth and metabolism of mixotrophic microalgae.

A combination of both phosphorus and nitrogen in one unit is very advantageous; therefore, a source of nitrogen and phosphorus should be added to the culture, in order to obtain high levels of productivity. Fertilizers seem to be an acceptable option; they can be used as a source of nutrients, as they contain nitrogen and phosphorus (Posten and Schaub 2009). Another option, which can substitute the use of fertilizers, is to grow microalgae in domestic wastewater instead of freshwater (Park et al. 2011). Domestic wastewater can provide the needed nutrients for microalgae growth, since it can contain high concentrations of nitrogen and phosphorus from nitrates and phosphates (Pittman et al. 2011). But prevention mechanism to avoid culture contamination should be put in place to reduce the risk of cell death and low biomass productivity rate.

14.6 Cultivation and Growth Medium

Cultivation of microalgae can take place in open ponds or in photobioreactors (PBR). Generally, the growing culture is directly exposed to the environment when using an open pond. It uses solar energy as the source of light needed for microalgae cultivation (Widjaja et al. 2009). In this system the temperature can be regulated by liquid evaporation. Paddle wheels are used in open race ponds in order allow a cost-effective gas or liquid mixing and/or circulation. They also allow to expose to light as many cells as possible for an effective photosynthesis (Cheng-Wu et al. 2001). Open pond systems are generally less expensive; their manufacturing requires lower cost material and less energy. However, open ponds are less effective in terms of light and temperature control. They require bigger area, and only a small number of microalgae species can be cultivated. There is a possibility of culture contamination including the production of low-density microalgae when using open ponds (Pulz 2001; Richmond 2004; Carvalho et al. 2006). Currently, an advanced form of ponds known as raceway ponds are being used because of their effectiveness in terms of biomass production rates. Raceway pond channels are constructed in concrete or made with compacted earth and possibly lined with white plastic to collect sunlight during daytime. Broth is harvested before the paddle wheel after the circulation loop is completed. The paddle wheel operates all the time to prevent sedimentation. Raceway ponds are operating since the 1950s. Figures 14.1a and 14.1b are examples of raceway ponds used on a site for microalgae cultivation.

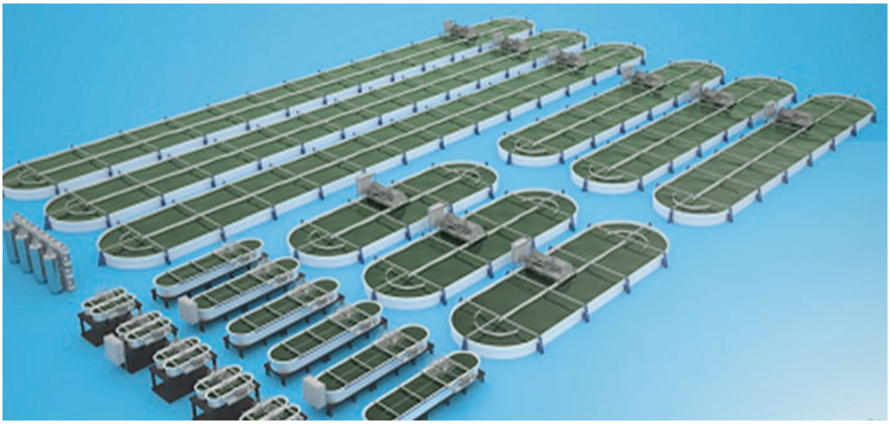


Fig. 14.1a Mobile raceway ponds for microalgae cultivation

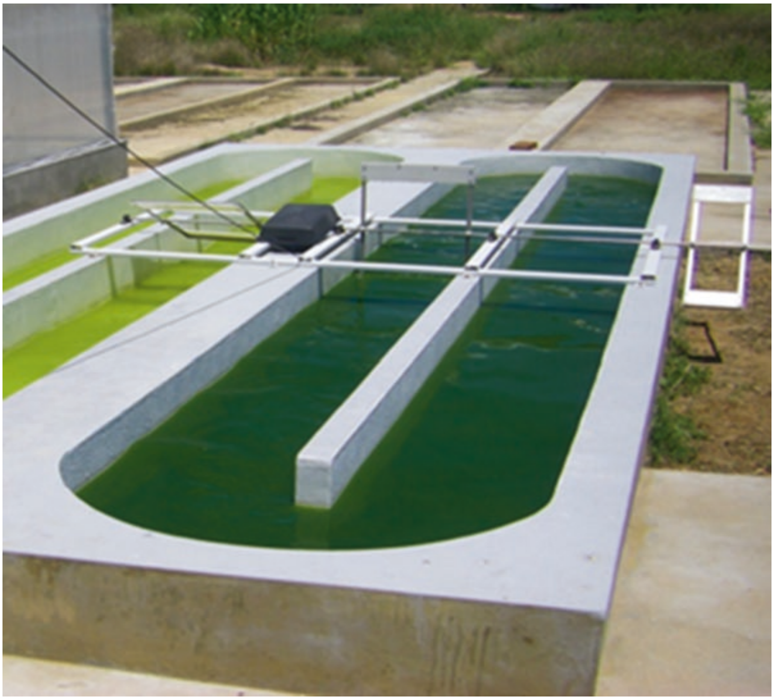


Fig. 14.1b Built-in raceway ponds for algae cultivation

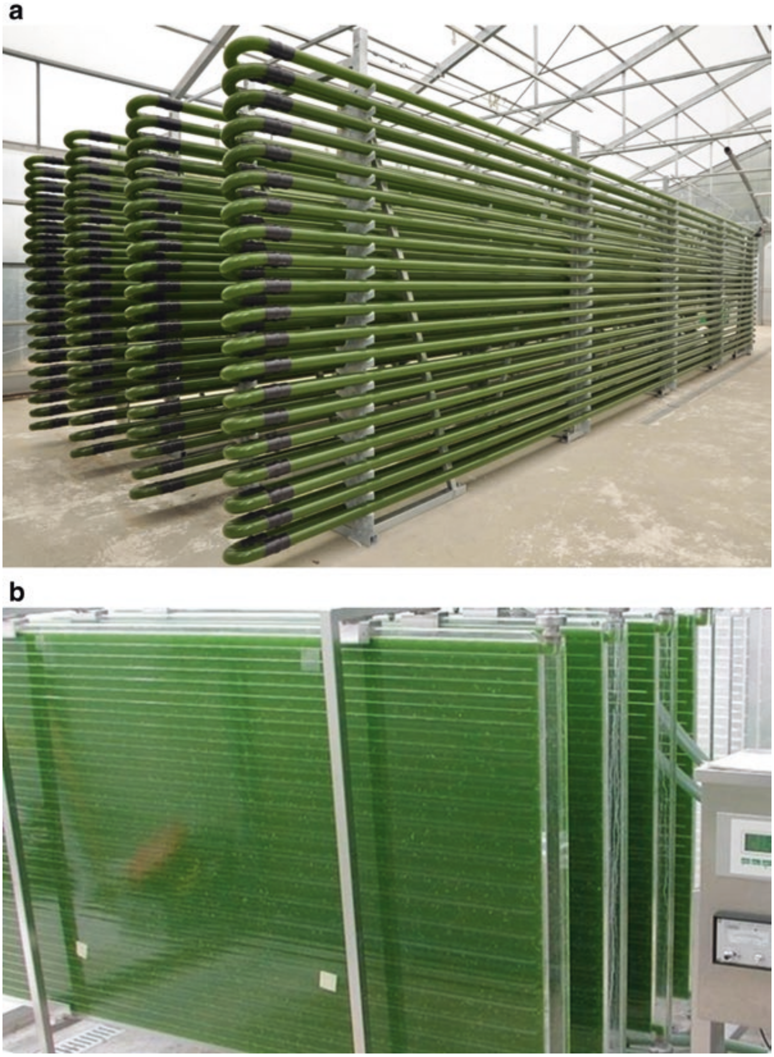
Photobioreactors are closed units generally operating in commercial or large scales for microalgae biomass cultivation. Microalgae growth or cultivation process should be meticulously monitored in order to produce more biomass and achieve precise biological modifications (Richmond 2004; Cheng-Wu et al. 2001). Their handling is easy compared to open ponds when it comes to gas and liquid mixing or mass transfer process. Photobioreactors are efficient systems in terms of energy consumption; they also use effectively the cultivation area (Carvalho et al. 2006; Sierra et al. 2008). They consist of arrays of straight tubes of 0.1 m or less in diameter to allow an effective penetration of light. Also, the limited diameter is meant to increase the biomass productivity. Generally, the tubes are always oriented north–south in order to maximize the sunlight penetration in the culture. In a characteristic arrangement, the transparent tubes are positioned in a parallel configuration as presented in Figs. 14.2a and 2b. These transparent tubes are generally arranged in an identical way to a fence. This configuration aims to get a high number of tubes that can fit in a given area.

To supply nutrients to microalgae, wastewater especially municipal wastewater is known as a reliable source of nutrients for microalgae cells as mentioned earlier. This implies that microalgae can be used for wastewater treatment, accumulating contaminants by absorption and adsorption allowing the removal of unwanted substances in wastewater in order to get a clean effluent.

14.7 Potential of Microalgae Bioremediation of Wastewater

Generally, the treatment of domestic sewage aims to remove the pathogen and stabilize the contaminants in order to generate a clean effluent. Therefore, domestic wastewater must go through a series of treatment steps including preliminary treatment, primary treatment, secondary treatment and tertiary treatment. Its composition depends on many factors including the lifestyle in the environment where it is collected. Generally, domestic wastewater contains suspended solids, inorganic and organic substances. Organic compounds include proteins and amino acids as well as carbohydrates and lipids in the form of fatty acids. The main source of organic compounds is food, toilet, bathroom and kitchen wastes. Nitrogen is found in large quantities in these wastes. Therefore, it is obvious to conclude that nitrogen in domestic wastewater comes mainly from human wastes generated by household units. In other words, it has been reported that human waste provides the large amount of nitrogen found in domestic wastewater. Also, domestic wastewater contains inorganic compounds including ammonia, chloride salts, phosphates, potassium and heavy metals in low concentrations. Illegal disposal of pesticides constitutes on of the main sources of inorganic components in municipal wastewater. Phosphorus compounds in domestic wastewater may also originate from domestic human wastes. These include food and synthetic detergents.

Domestic wastewater also contains a large population of microorganisms, pathogens, emulsions and toxins such as pesticides, poisons and herbicides



Figs. 14.2a and 14.2b Photobioreactors used for algae cultivation

(Alshehri et al. 2014; Naushad et al. 2014). Generally, many algae species grow well in domestic wastewater. Many of these species have shown potential in bioremediation of wastewater because it is a conducive environment for species. It is offering a possibility of effective cultivation and growth because of to the presence of nutrients in large amounts. The uptake of nutrients and contaminants takes place by biosorption; they accumulate nutrients to allow effective growth (Bwapwa et al. 2017). The following are few examples of species that have proven to be effective in wastewater bioremediation using microalgae:

Chlorella is very effective when it comes to the removal of Pb(II) from any wastewater.

It has a high removal efficiency for N and P from domestic wastewater. It is also very effective regarding the removal of cyanide from wastewater. *Pithophora* sp. is very effective in the removal of malachite green dye from wastewater.

Scenedesmus abundans has the capacity to remove Cd and Cu in wastewater. Also, it is effective in the removal of cyanides from wastewater. *Sargassum muticum* can remove methylene blue dye from wastewater. *Spirulina* sp. is reported as an effective strain for heavy metal removal including Sb and Cr. *Botryococcus braunii* has shown potential for the removal of nitrogen and phosphorus. *Dunaliella salina* has the ability to remove heavy metals like Cu, Cd, Co and Zn. Also, it is among the best species for hypersaline wastewater treatment. *Ankistrodesmus* sp. has a great ability to absorb heavy metals; it is very effective in the removal of Hg, As and Se through methylation. *Micractinium* sp. removes effectively Zn and Cd from wastewater through biosorption; it is achieved with a train named *Micractinium pusillum. Pediastrum* sp. is known as an indicator of organic compounds in wastewater; the uptake process of organic contaminants in this case takes place through biosorption. However, these species have been used to production biofuel such as biodiesel. There is possibility to convert biodiesel to bio-jet fuel. Therefore, the production of aviation biofuel from algae species is technically possible.

14.7.1 Combination of Domestic Sewage Treatment and Biofuel Production: The Advantages, the Problematic and the Gap

As mentioned earlier domestic wastewater contains large amount of nutrients which are essential for microalgae growth. Consequently, an effective growth of microalgae cells will generate high amount of biomass to be used to produce bio-jet fuel or any other biofuel. Nutrient removal efficiency depends on the following: microalgae species, quality of domestic wastewater and operating conditions such as initial nutrient concentration, light intensity, nitrogen/phosphorus ratio and light/dark cycle. The protection of the growing culture against the predators should also be included. The use of microalgae for wastewater remediation has attracted many interests due to the efficient nutrient's removal ability from wastewater and biofuel production. Microalgae offer the advantages of significant biomass production rates, possibility of high lipid productivities, ability to bio-sequester carbon dioxide and high possibility to remove contaminants from domestic wastewater as mentioned before. The technology/potential of using microalgae to remove contaminants from domestic wastewater as well as the conversion to biofuel require more critical reviews to establish sustainable options. There is synergy taking place between wastewater and algae cells when they are together in the same environment as shown in Fig. 14.3. The synergy allows the growth of microalgae by the same

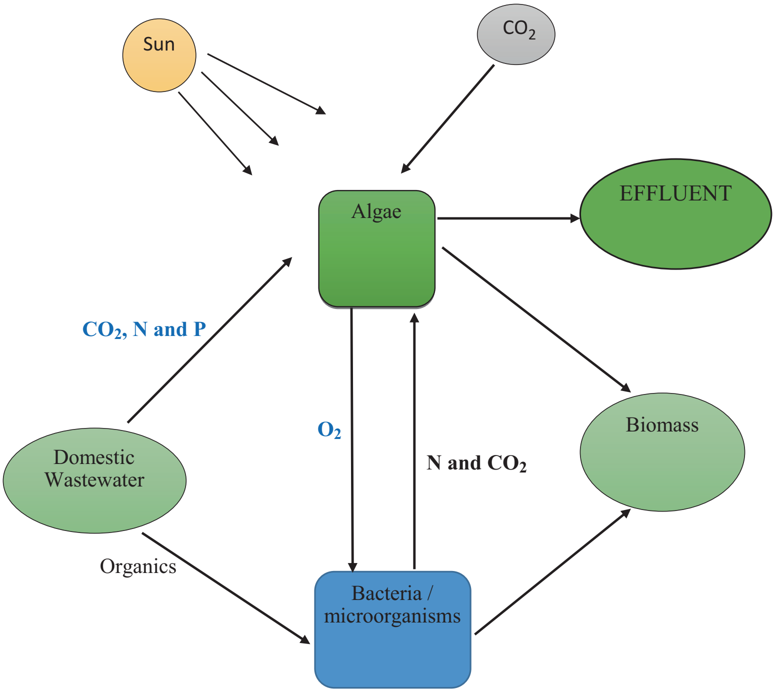


Fig. 14.3 Synergy between algae and bacteria in domestic wastewater for wastewater algae bioremediation and algae biomass production

time removal of nutrients by bioaccumulation takes place to get a clean effluent as mentioned earlier. Figure 14.3 shows the synergy between microalgae and bacteria in wastewater treatment process. In this synergy biomass is collected by harvesting after wastewater treatment and can therefore be used for biofuel production. The possibility to articulate between wastewater treatment, biomass and biofuel production can be very interesting in terms of its cost-effectiveness, energy-saving potential and maintenance. This can be a gap for future studies to analyse in details the combination involving biofuel production more especially jet fuel and domestic wastewater. Therefore, the dual application of microalgae for phycoremediation and the production of biomass in order to generate sustainable biofuels is a feasible option (Rawat et al. 2011). However, there is a need to adapt many parameters for a better articulation between bioremediation and biomass production for biofuel production in general and bio-jet fuel in particular. In this case modelling studies, process improvement and design, choice of species capable of producing high biomass and oil output while removing contaminants can be among the aspects to be studied.

14.7.2 Combining Algae-Based and Conventional Wastewater Treatments in One Unit

Algae-based treatment of wastewater can be included in the conventional treatment process as a secondary treatment to replace or complement the oxygen supply system in the conventional system. This way can be suggested as a new conceptual approach for wastewater treatment. The necessary oxygen to feed the microorganisms will be supplied by microalgae species. Microalgae will proceed by absorption and absorption for the removal of contaminants while supplying oxygen to the microorganisms or bacteria. Consequently, energy consumption will be reduced as the source of oxygen is the microalgae cells. Aeration process is a costly and energy demanding. It accounts for 45–75% of the total energy costs in the process of wastewater treatment (Rosso et al. 2008). However, the inability for microalgae to uninterruptedly generate the needed oxygen by microorganisms in order for them to accomplish their task can be a major challenge. Consequently, the treatment time will be longer than in a conventional treatment. Combining algae-based and conventional treatment as presented in Fig. 14.4 is an option that requires more studies because there a cost related to handling of algae biomass and maintenance to be considered. The figure presents the conceptual option suggesting the incorporation algae-based treatment into a conventional treatment plant to achieve the objectives of domestic wastewater treatment and produce biomass for conversion into algae-based fuel such as biodiesel and bio-jet fuel.

14.7.3 The Effectiveness of Algae Growth in Wastewater to Produce Biomass

An efficient growth of microalgae in domestic wastewater depends on many parameters. These parameters include the pH, temperature of the growth medium, the light intensity and salinity. Furthermore, effective algae growth relies mainly on critical parameters such N, P and organic carbon and CO_2. For instance, it was reported that the growth of microalgae in primary settled sewage wastewater increased significantly under long culture illumination periods with CO_2 addition. However, with increased temperature it was reported that the biomass productivity decreased (Pittman et al. 2011). Mostly, the main difference between domestic wastewater used as a growing media and other media is that there is a presence of high concentrations of N and P in domestic wastewater compared to other growing media. Most N is generally found in the form of ammonia. This can at high concentrations cause growth inhibition for algae species (Pittman et al. 2011; Konig et al. 1987; Wrigley and Toerien 1990). The presence of toxins is another threatening factor for algae growth in domestic wastewater. These toxins are mainly from degraded food, detergents and many other chemicals used domestically. Their presence can impact negatively on species growth, bacteria and other microorganisms. In addition,

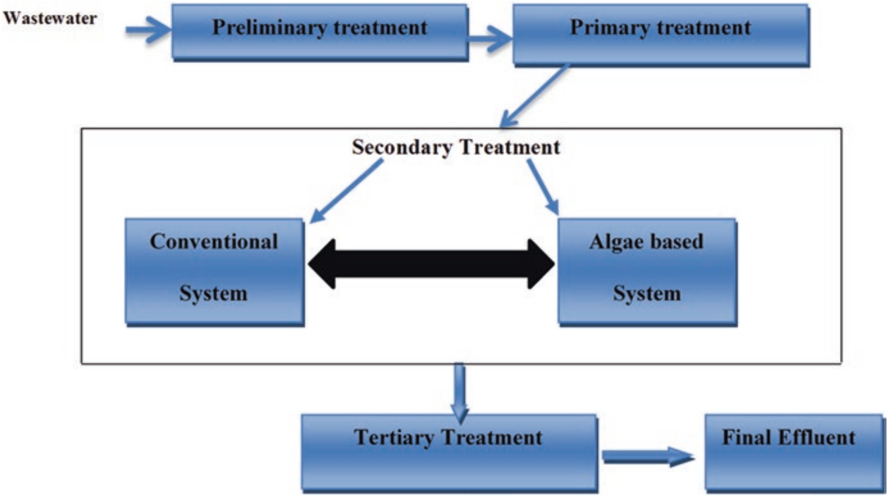


Fig. 14.4 Positioning algae-based into a conventional wastewater treatment plant

microorganisms in wastewater might tend to compete with microalgae for essential nutrients; consequently, the removal efficiency can be affected.

The initial density for microalgae in wastewater is probably one of the critical factors but not the only one that could influence the growth of the entire cells or biomass population (Lau et al. 1995). For instance, from a primary sewage treatment, *C. vulgaris* was used as a remediation species; over 90% and 80% removal efficiencies were, respectively, recorded for N and P (Lau et al. 1995). Therefore, the effective nutrient removal from domestic wastewater using microalgae is not necessarily depending on starting cell density. Wang et al. (2010) also focused on the growth of *Chlorella* in pretreated wastewater in addition to wastewater from three subsequent treatment phases. It was reported that many of the tested parameters such as N and P and heavy metals including growth rate remained almost unchanged before and after primary settling. However, it is important to emphasize on the facts that the quality of domestic wastewater and the site/area and environmental conditions where it is generated can have a significant influence in the variability of parameters before and after settling.

Also, the species type is another factor influencing growth effectiveness. It is related to the ability of the species to accommodate itself to the type of domestic wastewater, its composition and the environmental conditions. In this regard, unicellular chlorophytic microalgae species are particularly lenient to various wastewaters and effective when it comes to absorption/removal of nutrients from wastewater (Aslan and Kapdan 2006; González et al. 1997; Ruiz-Marin et al. 2010). Consequently, the species ability to survive in wastewater environment plays a vital role in the effectiveness of microalgae growth. For instance, *Chlorella vulgaris* is efficient than *Chlorella kessleri* at removing/absorbing N and P from wastewater, while *Scenedesmus obliquus* grows efficiently in municipal wastewater than

C. vulgaris (Ruiz-Marin et al. 2010). *Chlorella* and *Scenedesmus* are generally known as the major species in oxidation ponds (Masseret et al. 2000) and in high-rate algae ponds (Canovas et al. 1996). Overall, the effectiveness of algae growth will mainly depend on growth conditions, the nutrients, the nature of the species and the growth medium. These aspects will assist in producing sufficient biomass with lipid content that can be advantageous for conversion processes to produce a jet fuel complying with aviation standards (Table 14.1).

Table 14.1 Some examples of species used for domestic wastewater treatment

Wastewater type	Species and parameters	Removal efficiencies	References
Domestic wastewater	Species: *C. vulgaris*		Kshirsagar (2013)
	Parameters: COD, BOD, NO_3 and PO_4	80.64%, 70.91%, 78.08% and 62.73%, respectively	
Domestic wastewater	Species: *S. quadricauda*		
	Parameters: COD, BOD, NO_3 and PO_4	70.97%, 89.21%, 70.32% and 81.34%, respectively	Ayodhya and Kshirsagar (2013)
Domestic wastewater	Species: *Chlorococcum humicola*		Thomas et al. (2016)
	Parameters: BOD, TDS, TSS, TS, N, P	59%, 66%, 49%, 64%, 80% and 100%, respectively	
Domestic wastewater	Species: *Chlorella vulgaris*		
	Parameters: BOD, TDS, TSS, TS, N, P	67%, 67%, 60%, 67%, 84% and 100%, respectively	Thomas et al. (2016)
Domestic wastewater	Species: *Selenastrum* sp.	63%, 49%, 54%, 49%, 82% and 100%, respectively	Thomas et al. (2016)
	Parameters: BOD, TDS, TSS, TS, N, P		
Domestic wastewater (settled sewage)	Species: *Chlorella pyrenoidosa* and *Scenedesmus* sp.	More than 80% for both N and P	Tam and Wong (1989)
	Parameters: N and P		
Domestic wastewater	Species: *Botryococcus braunii* and *Chlorella vulgaris*	79.63% of the nitrogen and phosphorus	Sydney et al. (2011)
	Parameters: N and P		
Domestic wastewater	Species: *Scenedesmus* sp. ZTY1	Over 90% for N, 97% for P	Zhang et al. (2014)
	Parameters: N and P		

14.7.4 Growth of Microalgae in Municipal Sewage Wastewater

In a municipal sewage treatment, sedimentation is the first step known as primary treatment undertaken for solid removal. The sedimentation process is followed by a secondary treatment phase to achieve a complete removal of suspended and dissolved organics. Thereafter, tertiary treatment phase takes place; this phase involves disinfection for pathogen removal prior to discharge. The potential of microalgae to remove N and P can be explored in this phase. Microalgae are very effective regarding the removal of N and P in sewage wastewater because they are the main nutrients needed for microalgae growth.

It is a fact that microalgae cells supply oxygen to microorganisms and at the same time they also absorb contaminants from sewage wastewater; however, the challenge is the adaptation of species in the sewage environment. Various unicellular species are very tolerant to sewage effluent conditions, heavy metals and other contaminants more especially those of the *Chlorella* and *Scenedesmus* genera (Chinnasamy et al. 2010; Lau et al. 1995; Ruiz-Marin et al. 2010; Shi et al. 2007; Wang et al. 2010).

Many strains of *Chlorella* and *Scenedesmus* can provide high removal efficiency of up to 80%; for various cases complete removal of ammonia, nitrate and total P from secondary treatment can be achieved (Martınez et al. 2000; Ruiz-Marin et al. 2010; Zhang et al. 2008). Generally, many species have a significant removal potential for N and P as well as other substances when used as bioremediation agent for domestic sewage wastewater. Overall, algae growth is strongly related to removal efficiencies of nutrients and other substances. The higher the removal efficiencies, the more effective the growth of algae species in domestic wastewater. To have high removal efficiencies, optimal growth conditions must be well established, and the growing culture must be protected against inhibitor agents such as toxins and pathogenic bacteria.

14.7.5 Challenges Related to the Cultivation of Algae in Domestic Wastewater

In conventional wastewater treatment plants, nutrient removal process is generally less expensive for small scales. However, at large scales there are major technical and economic challenges that rise due to higher levels of contaminants in the effluent, large volume of effluents and energy consumption. Using existing municipal wastewater facilities and streams will reduce nutrient costs; on the other hand, it presents a high risk of introducing pathogenic bacteria, toxins, complex organic compounds or heavy metals into the biomass stream (Gnanasekaran et al. 2018; Pugazhendhi et al. 2018; Wilson et al. 2009). Limited knowledge is available regarding the artificial pond ecology or pathology; more investigations are very imperative in order to gain knowledge with regard to risk mitigation and remediation strategies for large-scale microalgae cultivation. It will also assist in culture stability, nutrients source scaling, monitoring productivity, sustainability and management, as well as water conservation, management and recycling (U.S. DOE 2010). Algae-based treatment for domestic wastewater can be much more effective in countries dominated by tropical climate. In these countries there is abundant sunlight throughout the year that can be conducive for microalgae growth. It is important to emphasize that climate and sunlight have a significant influence on microalgae growth and it is not easy to maintain the optimum for temperature. Additionally, there are biological and operational challenges that may occur during microalgae growth process. They can be due to culture contamination, auto-inhibition and grazing. There are ways to prevent contamination by using sterilization and ultrafiltration of the culture medium. With regard to grazing, this can be prevented by using chemical treatment. Other main challenges related to growth or cultivation of microalgae in domestic wastewater may include parameters such as light requirements, mixing, harvesting and oxygen depletion.

14.8 Harvesting Methods

Harvesting microalgae aims to collect the biomass needed for downstream processes. It is an important cost component, owing to the challenges involved in the entire process of jet fuel production. It is beneficial for algae processing industry to be informed on relevant harvesting techniques that are cost-effective, the challenges related to each option and the current efforts and solutions being attempted in order to overcome these challenges. Also, there are attempts to skip the harvesting process aiming to reduce the costs related to harvesting and drying. However, these attempts are not yet sustainable on large scale. Some major technologies commonly used for microalgae harvesting are centrifugation, filtration, sedimentation and flotation (Danquah et al. 2009; Chen et al. 2011). Table 14.2 summarizes the strengths and weaknesses of these techniques.

14.9 Algae Bio-Oil Extraction

There are three major compounds that can be extracted from microalgae biomass: firstly, lipids involving triglycerides and fatty acids; secondly, carbohydrates; and finally proteins. Lipids and carbohydrates are known as fuel precursors (e.g. gasoline, biodiesel and jet fuel), and proteins can be used as raw materials for the manufacturing of by-products. Many challenges related to bio-oil extraction are linked to scaling up of integrated extraction systems. Although many analytical techniques exist and they are being used up to date, it is challenging to optimize extraction

Table 14.2 Strengths and limitations of harvesting techniques

Harvesting technique	Strengths	Limitations
Filtration	Less expensive, wide variety of filters and membranes available	Require frequent backwashing and time-consuming. Totally depending on species; very suitable for large algae cells. Clogging or fouling an issue to be addressed
Flotation	Cost-efficient and more rapid than sedimentation	Use of chemical
		Depend on suspended particles
		Less reliable, algae species specific
		High capital and operation costs
Centrifugation	Quick	Expensive due to high energy consumption and high capital costs
	Highly efficient	
	Good recovery	
Sedimentation	Low costs, potentially useful for first stage in order to reduce energy input and costs of subsequent stages	Slow separation, final concentration may be low
Microfiltration/ ultrafiltration	Capable to handle nannochloropsis cells, very efficient and can reach up 98% dewatering	High operating costs and membrane fouling
	Can be used as pretreatment prior to centrifugation	

Adapted from Grima et al. (2003), Christenson and Sims (2011)

systems that will exhibit low energy consumption than the one contained in the algae cells. This is due to significant energy demand associated with both harvesting, drying algae biomass and separation of by-products. Investigations are still underway aiming to develop options that will help to bypass bio-oil extraction, though these are also subjected to a number of unique scale-up challenges. This can be the case of catalytic processes such as biomass gasification and Fischer–Tropsch.

Lipid extraction from microalgae biomass is largely more focused on lab-scale processes. This has a weakness of serving more the purpose of analytical processes instead of focusing on biofuel production. However, the extraction process determines the oil output or recovery needed for downstream processes. The more efficient is the extraction, the more oil is collected for conversion processes. Solvent-based extraction is the most undertaken technique till date to get bio-oil out of microalgae cells because of its cost-effectiveness. The mixture of various solvents is also used for lipid extraction. The method developed by Bligh and Dyer (1959) has been a well-known co-solvent extraction procedure using the mixture chloroform–methanol–water in 1:1 ratio with the algae biomass. Chloroform will assist in extracting the following fractions: saponifiable lipids and the unsaponifiable lipids such as pigments and lipoproteins. Also, other lipid and non-lipid contaminants will be also extracted using chloroform (Fajardo et al. 2007). Other combinations of co-solvents are suggested for lipid extraction: the case of hexane/isopropanol used for tissue (Hara and Radin 1978), dimethyl sulfoxide/petroleum ether used for yeast (Park et al. 2007), hexane/ethanol for microalgae (Cartens et al. 1996) and hexane/isopropanol used for microalgae (Nagle and Lemke 1990). The hexane system has been recommended in many cases. A layer will be formed between hexane and alcohol creating two phases with water addition; consequently, there will be an improvement of downstream separations (U.S. DOE 2010). Also, less volatile and toxic alcohols such as ethanol and isopropanol are suggested instead of methanol. A single solvent can also be used for extraction depending on its effectiveness in extracting oil from the biomass. The latest study using only one solvent was completed by Kanda et al. (2012) using dimethyl ether (DME). In this process crude bio-oil was extracted from blue-green microalgae. DME molecules disperse inside cells through cell walls and bind strongly to the oily components. Its boiling point is 25 °C but it liquefies under 20 °C. DME is recovered as vapour only through depressurization.

14.10 Origin of Petroleum Crude Oil and Comparison with Algae Crude Oil

Algae bio-crude oil from various strains is similar in quality to petroleum crude oil (Hannon et al. 2010). Fossil crude oil comes from algae in marine environment or old algae deposit made of liquid hydrocarbons (EIA 2009). On average 85% w/w of oil is made of C, 10–14% of oil is H_2, O_2 represents only 1–2%, and S represents up to 4% of the oil total weight (Hunt 1996). Petroleum crude oil comes from kerogen, a compound present in sedimentary rocks within marine environment. It is formed after a sequence of biochemical and chemical reactions named diagenesis and catagenesis (Gize and Manning 1993). Kerogen is converted into fossil crude oil under defined conditions of pressure and temperature. It is mainly made up of algae, organic compounds, bacteria and plant material. Most of these compounds present in crude petroleum oil are also found in crude algae bio-oil (JK Bwapwa et. al 2018). Consequently, there is a possibility to use crude bio-oil in the same processing plant producing conventional jet fuel to produce algae-based jet fuel (Bwapwa et al. 2017).

14.11 Species with Potential to Be Used for Algae-Based Jet Fuel

Table 14.3 presents the bio-oil outputs from various microalgae species. The quality of bio-oil generated from these species is appropriate for any biofuel as well as bio-jet fuel. They can be successfully cultivated in domestic wastewater to produce the biomass needed for conversion processes.

Table 14.3 Output in terms of oil content for some algae species

Microalgae species	Bio-oil output per mass of dry biomass [%]
Botryococcus braunii	25–75
Nannochloropsis sp.	31–68
Schizochytrium sp.	50–77
Neochloris oleoabundans	35–54
Nitzschia sp.	45–47
Ankistrodesmus TR-87	28–40
Chlorella sp.	29
Chlorella protothecoides (autotrophic/ heterotrophic)	15–55
Crypthecodinium cohnii	20
Cyclotella DI-35	42
Dunaliella tertiolecta	36–42
Hantzschia DI-160	66
Nannochloris 31	6–63
Neochloris oleoabundans	35–54
Nitzschia TR-114	28–50
Phaeodactylum tricornutum	31
Scenedesmus TR-84	45
Stichococcus	9–59
Tetraselmis suecica	15–32
Thalassiosira pseudonana	210–310
Euglena gracilis	14–20
Hormidium sp.	38
Phaeodactylum tricornutum	20–30
Pleurochrysis carterae	30–50
Chlamydomonas reinhardtii	21
Prymnesium parvum	22–38
Tetraselmis suecica	15–23
Chlorella emersonii	28–32
Hormidium sp.	3.8
Chlorella pyrenoidosa	47
Chlorella vulgaris	14–22
Crypthecodinium cohnii	20
Dunaliella tertiolecta	36
Dunaliella salina	6
Dunaliella primolecta	23
Cylindrotheca sp.	16–37
Phaeodactylum tricornutum	20–30
Pleurochrysis carterae	30–50
Scenedesmus dimorphus	16–40
Scenedesmus obliquus	12–14

Adapted from Chisti (2007), Georgianna and Mayfield (2012), Brennan and Owende (2010))

14.12 General Requirements and Compliance for Jet Fuel

A complying jet fuel should provide necessary energy for aircraft propulsion and avoid freezing at higher altitudes. Therefore, it must comply with technical and operational specifications. Furthermore, jet engines must be designed accordingly in order to operate under these specific requirements. Both the relatively slow rates for aircraft fleet renewal and the features of the aviation sector require that any jet fuel should be produced from high-quality crude oil. Also, refinery or conversion processes from crude oil to jet fuel should be cost-competitive. They also have to enable the production of a complying jet fuel to establish aviation standards which are expected to be highly competitive on the market. This kind of jet fuel is defined as a 'drop-in' jet fuel. It is the alternative version of jet fuel needed on the market to compete with the conventional jet fuel. On the other side, a 'non-drop-in' jet fuel implies that new aircrafts and infrastructures would require an important investment in a supply chain system to be independent from conventional jet fuel. Additionally, the engine technology should be specifically designed for the 'non-drop-in' jet fuel. Currently, it is a fact that no manufacturer of aircrafts or engines is ready to restrict the use of their equipment to a particular fuel or way of operating or even developing new equipment to accommodate a new fuel. This will require new studies and new investments from the fuel manufacturer and could be time-consuming. Therefore, this suggests that in the near to mid-term, efforts should be made to produce alternative fuels which are 'drop-in'. To keep using the same equipment or engines without any modification, this is an ideal situation. Nevertheless, 'non-drop-in' jet fuels should not be automatically rejected, but they have to be carefully evaluated in terms of their quality and performance and finally improved substantially in order to comply with the standards and meet the market expectations. Consequently, an elaborate improvement approach should be undertaken thoroughly with regard to parameters such as efficiency, environmental impacts and costs.

Producing a microalgae-based jet fuel totally compliant to stringent regulations defined by standard bodies is one of the biggest challenges to be overcome. Compliance focuses mainly on properties related to physico-chemical parameters and combustion and kinetic aspects (JK Bwapwa et al. 2017). Generally, the composition of conventional jet fuel is structured as follows: 20% paraffin, 40% isoparaffinic, 20% naphthenes and 20% aromatics (Blakey et al. 2011). However, additives are mixed to the conventional jet fuel in order to get a compliant final product matching with the stringent standards.

Compliance also implies that algae-based jet fuel must perform as a 'drop-in' substitution or support for the conventional jet fuel (Bauen et al. 2009). Table 14.4 presents ASTM limits and various ASTM methods used to perform some physico-chemical tests required for jet fuel compliance.

Table 14.4 Some ASTM standards used for jet fuel

Parameter	Unit	ASTM D1655 limits	Method
Density @15 °C	g/ml	0.775–0.840	ASTM D7042
Viscosity @- 20 °C	Cost	8 (maximum)	ASTM D445
Flash point	⁰C	38 (minimum)	ASTM D93
Water content	%	Nd	ASTM D6304
Total acidy	Mg KOH/g	0.015(maximum)	ASTM D3242
Total sulphur	%	0.3 (maximum)	ASTM D4294
Net heat of combustion	MJ/kg	42.8 (minimum)	ASTM D4868
Freezing point	⁰C	-40° C (maximum)	ASTMD D2386
Conductivity	pS/m	50–600	ASTM D2624

14.13 Current and Future Challenges

A part from the compliance and sustainability issues which are also challenging aspects, the other major challenges faced by algae-based fuels are biological, chemical and mechanical. Biological challenges are related to strain or species ability to grow effectively and to produce biomass and lipids. Therefore, the selection of the strain is regarded as one of the key aspects because of its link with lipid content, and also the nature of strain/species could have a direct influence on lipid biosynthesis, biomass productivity and the type of lipids produced (Eloka-Eboka and Inambao 2017). Chemical challenges are related to oil extraction with solvent use, operating conditions of transesterification reaction, the process of chemical harvesting, water quality and removal of contaminated constituents in water or wastewater used for microalgae growth (Hannon et al. 2010; Gerbens-Leenes et al. 2009; Bwapwa et al.,2017).

Mechanical challenges focus on equipment maintenance and performance related to cultivation equipment, harvesting systems, biomass drying and oil extraction equipment such as oil press or impeller (Hannon et al. 2010). Process optimization and modelling of relevant parameters related to these challenges will also assist to overcome them. Table 14.5 described further details on the main challenges recorded at each step of the production regarding algae-based fuels. These challenges are part of the main issues faced by algae-based fuel producers. They constitute the basis for research and development in the current context to improve and enhance the sustainability of algae-based fuels including bio-jet fuel from algae.

14.14 Proposed Process for Conversion of Algae to Jet Fuel from Wastewater

A set of processes can be explored to convert microalgae crude bio-oil into jet fuel. Prior to conversion processes, sufficient biomass should be produced via cultivation of microalgae under defined operating conditions including temperature, light

Table 14.5 Summary of the main challenges encountered on each process step of microalgae jet fuel production

Process step	Research and development challenges
Algae biology	Choice of relevant strains with high lipid content
	Development of small scale with high-throughput screening technologies
	Development of a relevant database and collection of existing strains with detailed characterization
	Investigation of genetics and biochemical ways for production of fuel precursors
	Improvement on strains for desired criteria by gene manipulation techniques and breeding
Algae cultivation	Investigation of cultivation approaches depending on the species nature
	Achievement of stable and robust cultures at commercial scale
	Optimization of algae productivity of fuel precursors
	Development of a sustainable and cost-effective models for water and land use and nutrients
	Identification and solving environmental impacts and risks
Harvesting and dewatering	Investigation of cost-effective harvesting process (centrifugation, sedimentation, flocculation, filtration, dissolved air flotation, microfiltration, etc.)
	Reduction of harvesting energy intensity
	Lowering the capital and operating costs
	Assessing each harvesting option in terms of compatibility and sustainability
	Development of new harvesting technologies to compete with the existing ones
Extraction and fractionation	Investigating and optimizing various approaches (sonification, microwave, solvent extraction, etc.)
	Minimizing and optimizing the process energy intensity
	Investigating recycling mechanisms to minimize wastes generated after bio-oil extraction
	Addressing scaling challenges due to operating parameters such as temperature, pressure, carrying capacity, separations and side reactions
Fuel conversion	Investigating on various approaches for sustainable processes to get jet fuel from microalgae (thermochemical, catalytic conversion, biochemical conversion, etc.)
	Minimizing contamination of the final product and reaction inhibitors
	Minimizing process energy consumption and carbon emissions over life cycle
	Achieving high conversion rates under scale-up conditions

Compiled from Chisti (2007), Georgianna and Mayfield (2012), Brennan and Owende (2010), Larkum et al. (2012)

intensity, salinity and pH depending on the species/strain type and nature as mentioned before. The cultivation process should incorporate the species genetic modification which is vital for lipid content increase. Conversion processes are undertaken after biomass harvesting and/or drying. Currently, there are numbers of conversion processes that can lead to jet fuel production from algae biomass. Some of the

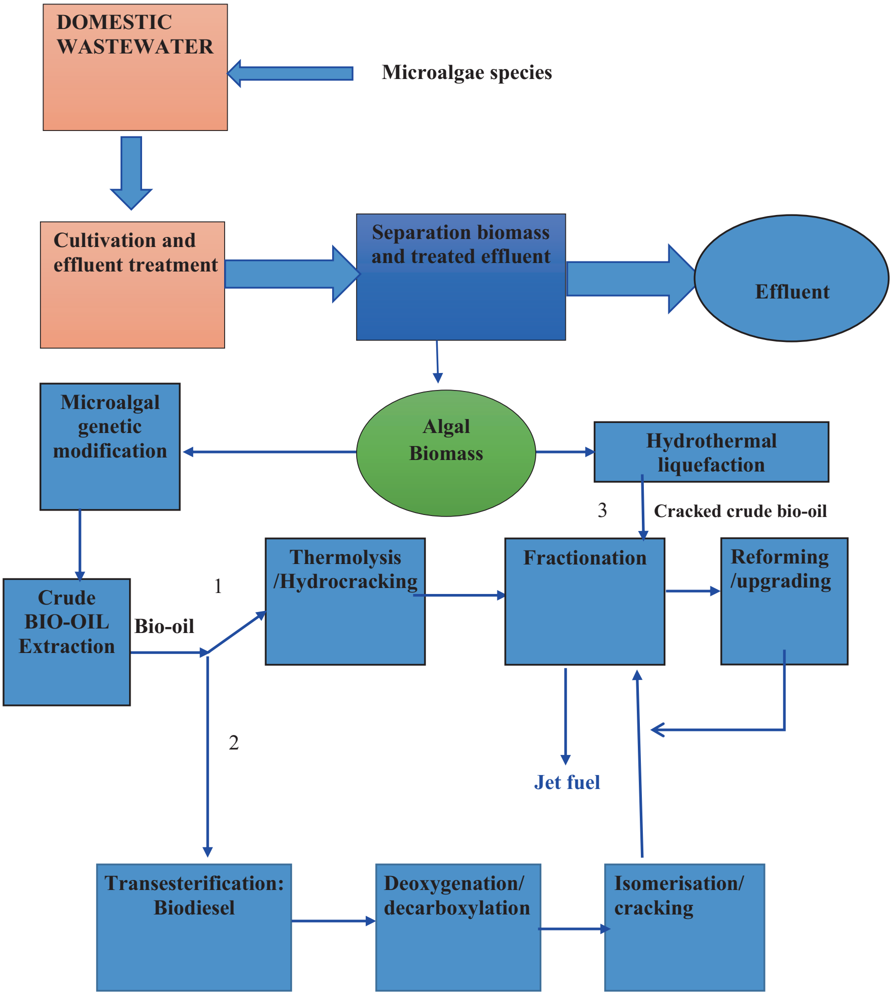


Fig. 14.5 Conceptual scheme to produce jet fuel from microalgae-based wastewater treatment

ground-breaking processes or techniques are patented and remain under the private domain. Figure 14.4 is the suggested model including both domestic wastewater treatment and bio-jet fuel production. Conventional wastewater treatment can be combined with algae-based wastewater treatment as suggested before. The generated algae biomass should be collected after treatment and be used for conversion processes. This collection should be done in a way that microorganisms are not taken away by the algae biomass. Figure 14.5 presents a conceptual scheme involving all the processes that are essential to generate jet fuel from domestic wastewater. The feasibility of this combined system should be undertaken in details specially in terms of costs and algae cultivation. From this concept not only jet fuel can be produced but other lighter fractions such as naphtha, biogasoline and diesel distillate depending on carbon chains found in the bio-crude oil from algae.

This conceptual process suggests three routes after recycling wastewater: The first is similar to a petrochemical process involving cracking, fractionation, reforming and upgrading. The second route is the biodiesel option which involves deoxygenation and decarboxylation, isomerization or cracking and finally the fractionation to get the relevant fractions for jet fuel. This option while technically sound is still costly and energy demanding. The third route is the hydrothermal liquefaction to produce cracked crude bio-oil ready for fractionation.

14.15 Various Conversion Processes to Be Used for Algae Biomass into Jet Fuel

14.15.1 Hydrothermal Liquefaction

Thermal depolymerization process for the conversion of wet biomass into crude bio-oil at moderate temperature and high pressure. The concentration of wet algae should not be less than 20 wt % solids. This slurry is hydrothermally treated in subcritical water, at a pressure range of 2000–3000 psia under temperature varying between 300 and 350 °C. The reaction temperature dictates the reactor pressure (Biddy et al. 2013). Hydrothermal liquefaction (HTL) is a very promising technology for any biomass into biofuels. The fast reaction using wet feedstocks without lipid content restriction makes it cost-effective and reliable. This makes HTL a suitable process for conversion of algae biomass into crude bio-oil. The chemical reactions that take place during the hydrothermal treatment are currently part of many studies; and the effect of main process variables on the liquefaction process is being also studied. These process variables include parameters such as temperature, heating rate, holdup time at the maximum temperature, biomass concentration in the water suspension, biochemical and elemental compositions of the microalgae, use of catalysts, etc. Bio-oil from HTL process requires additional catalytic processing for oxygen and nitrogen removal. Similarly, sulphur removal also takes place, but then it is found in the HTL bio-oil to a very low concentration. In this process no energy is spent for drying the algae biomass, the slurry is channelled straight into the reactor, and the crude bio-oil is produced without using a solvent after separating it with biochar. This process can be used in lieu and place of bio-oil extraction. However, HTL process requires an improvement of catalyst performance and the reduction of operating costs to be more efficient.

14.15.2 Biomass Gasification and Fischer–Tropsch Integrated Process (BG–FT)

In this technology there is a combination of CO and H_2 produced from coal, natural gas or biomass during gasification, and thereafter Fischer–Tropsch (FT) process turns these gases into a synthetic lubrication oil and synthetic fuel. Briefly, in this integrated process, biomass is gasified, and the generated bio-syngas is used for FT synthesis to generate long-chain hydrocarbons in order to be converted to fractions such as green diesel and jet fuel (Boerrigter et al. 2003). Biomass gasification and Fischer–Tropsch integrated process (BG–FT) can assist in deriving more varied forms of energy from the thermochemical conversion of biomass than conventional combustion. FT uses cobalt-based or iron-based catalysts; it is a well-established technology that can be combined with gasification process. The use of cobalt-based catalysts allows high oil output compared to iron-based catalysts at high conversion level. This is making cobalt the most appropriate catalyst (Van Steen and Claeys 2008). The bio-syngas collected from biomass can be H_2 deficient. Therefore, steam and O_2 are used as gasification units to improve the H_2 content in the syngas. Although the technology is promising for algae biomass conversion to jet fuel, this integrated process presents some weaknesses such as high oxygen and water content for the produced fuel, and it is requiring intensive impurity removal, control and adequate wastewater management approach. There is need for product separation and upgrading when using this technology to produce jet fuel.

14.15.3 Pyrolysis

This is a thermochemical process used to break down long carbon chains in shorter ones for any organic product at higher temperatures in very short amount of time. In this process, the oil is exposed to high temperature without oxygen. Different new molecules are obtained after a series of chemical and physical changes. Fast pyrolysis is achieved at temperatures between 400 and 600 °C in very short periods of time. Fast pyrolysis can yield up to 80% (in weight). Zeolite is used as catalyst during the process to improve the quality of oil.

The catalyst can cause the increase of aromatic content and allows the decrease of O_2. The catalytic pyrolysis generates outstanding quality oil with less or no upgrading processes. Consequently, it is a cost-effective process when compared to the non-catalytic (Venderbosch and Prins 2010). This process can be advantageous for microalgae biomass provided that the biomass is completely dried prior to pyrolysis. Drying is a supplementary cost to be taken into consideration. Pyrolysis readiness for biomass does not need to be proved anymore. It has also successfully been used to produce fossil-derived fuels. However, there is slow commercialization of this technology because of the weak demand for the crude bio-oil.

14.15.4 Cracking, Reforming and Upgrading

During cracking large hydrocarbon molecules are broken down into smaller alkane molecules. These small or short molecules are needed for fuel production. Fractions with long molecule chains are vapourized and exposed to hot catalyst for breaking into small chains. In this process temperature and catalyst play a very important role in making the breaking very effective. The effect of pressure during the process is not very significant compared to temperature and catalyst; however, it is still also needed during the process.

There are many types of cracking processes which can be used for algae biomass or any biomass; these processes include isomerization cracking, hydrocracking, thermal cracking, fluid catalytic cracking and steam cracking. These processes depend on the type of biomass used or oil to be produced. Hydrocracking is one of the most used processes for biomass product; it is a process achieved in two steps. It is merging catalytic cracking and hydrogenation, where heavy feedstock is fractured by the catalytic action of H_2 to generate required fractions. Generally cracking process uses moderate pressure, high temperature and a catalyst to achieve the breaking down of hydrocarbon chains. The pressure range is wide and depends on the application, and the temperature range is generally between 200 and 500 °C depending on the type of oil or biomass and the type of the cracking process. However, it is important to stress on the fact that the temperature can go beyond this range depending on the cracking-type process. The upgrading process is achieved via fluid catalytic cracking; during the process the heavier- or higher-boiling fractions from the crude oil distillation are upgraded by converting them into lighter- and lower-boiling, more valuable products. Reforming is a catalytic process allowing the conversion of low octane distilled from crude oil into high-octane liquid named reformates. It is also an aromatization process in which the conversion of open-chain hydrocarbons or cycloalkanes into aromatic hydrocarbons with equal number of carbon is completed with the assistance of a catalyst.

14.15.5 Deoxygenation and Decarboxylation

Deoxygenation is a chemical reaction that allows the removal of oxygen from a molecule. The process uses hydrogen and metal catalysts for deoxygenation of C-O bonds which are the most found in algae crude bio-oil. Decarboxylation is a chemical reaction characterized by the removal of a carboxyl group and the release of

CO_2. Large amounts of oxygen and CO_2 are removed from the bio-oil after decarboxylation; this reduces further the carbon footprint of bio-oil. Both are catalytic processes and are conducive to algae biomass; however the operating costs are still high. Algae crude bio-oil contains high level of oxygen which can be disturbing for conversion processes. They are also used for algae bio-oil that has been transesterified (biodiesel) in order to remove methyl esters and allow a suitable conversion of bio-oil into jet fuel.

14.15.6 Transesterification

Transesterification consists of producing biodiesel from bio-oil. Once biodiesel is produced, decarboxylation and deoxygenation can be used to generate high-purity jet fuel (Huntley and Redalje 2006). Decarboxylation or deoxygenation of methyl esters improves the jet fuel energy density. Also, the process helps to remove methyl esters which are contaminants in jet fuel. Isomerization cracking is used afterwards to break down large hydrocarbon chains into small alkanes. This will assist in decreasing the higher freezing point of cracked bio-oil to the one required for the jet fuel (Huntley and Redalje 2006). Usually, algae-based biodiesel has higher flash point, higher freezing point, higher density, lower kinematic viscosity and higher O_2 content compared to the ASTM requirements for aviation fuels. It is technically feasible to combine transesterification, deoxygenation and decarboxylation to produce jet fuel from microalgae, but the entire process is very expensive (Huntley and Redalje 2006). This option has not yet reached the maturity to be commercially viable.

14.15.7 Fractional Distillation

This process aims to separate light-end, middle-end and heavy-end carbon fractions based on their boiling points. Carbon fractions are separated by heating them to a temperature at which one or more fractions of the mixture will vapourize. This will be followed by the condensation of vapour phase to produce the required liquid fuel or substance.

Jet fuel is made of middle-end carbon fractions (C14 to C16); for algae bio-oil there is temperature range at which it is possible to collect these fractions. The temperature range begins from 70 °C, and the end point is around 250 °C at atmospheric pressure. This process is among the most important one during the process of producing any fuel. It plays an important role on the purity of the fuel. There is also a vacuum distillation which is used to further distil the residue bio-oil from the bottom of the crude oil distillation unit. It is performed at a pressure below atmospheric pressure. This operation is undertaken after upgrading process.

14.16 Conclusions

The potential to produce renewable energy from microalgae has reached a considerable interest at the present time; however, there is a need for further optimization of mass culture conditions and operating conditions for conversion processes to make microalgae bio-jet fuel economically viable and sustainable. Sewage wastewater can possibly deliver cost-effective and sustainable environment for growth in order to produce algae-based jet fuel in particular and other algae-based fuels in general. There is a potential in combining microalgae-based wastewater treatment and jet fuel production from the generated biomass after sewage treatment. It can happen with nutrient removal and jet fuel production in the same setup provided that operating conditions are well established and the design of the infrastructures is convenient to the type of application. This review has discussed various aspects related to potential benefits and limitations of using domestic wastewater as resource for cost-effective bio-jet fuel production.

Microalgae are known to grow faster in water, and they contain essential compounds that can be utilized for biofuel production. Domestic wastewater being rich in nutrients needed by microalgae can be used as medium for growth, while nutrients and contaminants are being absorbed by microalgae species. There many advantages to use microalgae for wastewater treatment and produce bio-jet fuel out of the biomass produced during treatment. This option can be viable, but wastewater should be well protected from contamination created by harmful toxins and toxic substances that can prevent the operation of microalgae cells in reducing the pollution load from wastewater. Using microalgae for domestic wastewater treatment will reduce the costs related to oxygen production and maintenance. Microalgae are effective in removing nitrates, phosphates, heavy metals, COD and BOD. Also, microalgae strains are viewed as promising alternative because they contain extensive fatty acids and lipids. There is possibility to attain over 60% lipids after genetic modification achieved by nutrient starvation. Microalgae have ability to grow briskly and synthesize higher quantities of TAGs and high-value polyunsaturated fatty acids such as eicosapentaenoic acid that can be converted in to the bio-jet fuel for the aviation industry. Jet fuel has 14–16 atoms of carbon, and triacylglycerol is known for high content of short-chain fatty acids. This key feature of this species allows exploring the possibility of producing bio-jet fuels from microalgae. Production of bio-jet fuel from microalgae requires production system to grow microalgae. The various aspects related to microalgae cultivation in open systems like ponds and closed system like photobioreactors were highlighted. Open pond systems are less expensive and require less energy, but the major drawbacks are less-efficient temperature control, usage of light, relatively larger area and risk of contamination. Currently high-rate algae ponds such as raceway ponds are used to remediate many weaknesses observed from open ponds. They have showed great reliability and promise for microalgae cultivation. Photobioreactors are easy to be handled compared to open pond systems for mixing and mass exchange of gas or liquid; however, a major challenge is the use of artificial lighting. In industrial scale, volumes of culture medium to be prepared and dealt with are highly expensive, particularly when artificial seawater is used. Many environmental factors like light, temperature, pH, salinity and nutrients determine the biochemical content of cultivated microalgae. These factors have an effect on photosynthesis and thus carbon fixation. According to environmental conditions, microalgae modify their lipid biosynthesis pathways in nutrient-deprived conditions. The cultivation of microalgae is followed by the separation biomass from the media and subsequent lipid extraction. Harvesting of microalgae involves the extraction of triglycerides by dewatering, drying and then solvent extraction. There is no fundamental harvesting method in the current situation with perfect advantages of time, energy and cost. Some of the major technologies commonly used are centrifugation, sedimentation filtration, flocculation and flotation. Production of bio-jet fuel from microalgae requires cost-effective methods for commercial-scale cultivation and sustainable harvesting systems. It is clear that technological development is still needed for better harvesting techniques. Possible biotechnological developments in this procedure might find an appropriate and economical harvesting process. Efficient method for lipid extraction is another key factor for bio-jet fuel production. Transesterification is used in the conventional biodiesel production techniques, but now there are many options available for extraction of neutral lipids. Alternative techniques such as catalytic megaspores, biomass hydrothermal liquefaction and gasification as well as pyrolysis have been postulated. Although the total biofuel production improves significantly when both polar and non-polar lipids are used for fuel production, some studies regarding this strategy making use of total lipid content for production of biofuel by direct transesterification has demonstrated promising results. Bio-jet fuel production from *Nannochloropsis* could be more cost-effective in the foreseeable future with aid of modern harvesting technologies and extraction techniques.

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