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Ram Naresh Bharagava *Editor*

Emerging Eco-friendly Green Technologies for Wastewater Treatment

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This book is truly dedicated to my parents for their unfailing patience, contagious love, forgiveness, selflessness, and endless support, my wife for trusting and believing me, and my kids for always being a hope to move forward in life.
Ram Naresh Bharagava

Preface

Environmental pollution has become one of the serious problems of the current scenario worldwide. Environmental safety and sustainability with rapid industrialization is also a major challenge. Environmental pollutants are mainly organic and inorganic in nature and are released in the environment through natural and anthropogenic activities. Organic pollutants mainly include pesticides, phenolic compounds, chlorophenols, petroleum hydrocarbons, azo dyes, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), organometallic compounds, persistent organic pollutants (POPs), etc., whereas inorganic pollutants include a variety of toxic and non-biodegradable heavy metals such as cadmium (Cd), chromium (Cr), lead (Pb), arsenic (As), and mercury (Hg). Among the different sources of environmental pollution, industrial wastewaters are mainly considered as the major sources of environmental pollution. The untreated/partially treated wastewaters discharged from various industries contains potentially toxic and hazardous organic and inorganic pollutants, which cause the pollution of soil and aquatic resources including groundwater and severe toxic effects in humans, animals, and plants. The governments around the globe are strictly advocating for the mitigation of environmental pollution. Hence, the removal/elimination of pollutants from the contaminated environment is utmost important for environmental safety and to promote the sustainable development of our society with low environmental impacts.

Various approaches are being applied for the removal of toxic and hazardous pollutants from contaminated environments. Physicochemical approaches are commonly used for the treatment and management of contaminated environment, but these approaches are environmentally destructive in nature due to generation of secondary pollutants, which is also a serious concern. Ecofriendly approaches such as bioremediation approaches can be a sustainable solution for the treatment and management of environment contaminated by a wide range of organic and inorganic pollutants. Bioremediation is an environment-friendly and cost-effective technique that uses microbes such as bacterial, fungi, and algae., green plants, or their enzymes to degrade/detoxify the toxic environmental pollutants from the polluted soils and aquatic resources. Bioremediation is recognized and approved by the United States Environmental Protection Agency as an ecofriendly solution for environmental management. The ecofriendly removal of pollutants from contaminated environments requires our increasing understanding of degradation pathways and regulatory networks to carbon flux for their degradation and detoxification, which is utmost important for environmental safety. Therefore, this book provides the comprehensive and up-to-date knowledge of eco-toxicological and health effects of various environmental pollutants and ecofriendly approaches for their degradation and detoxification for environmental management.

The main focus in this book relies on the eco-toxicological and health effects of various toxic and hazardous environmental pollutants such as toxic metals, pesticides, azo dyes, petroleum hydrocarbons, and a variety of toxic heavy metals such as cadmium and chromium released from natural as well as anthropogenic sources, their toxicological effects in environments, humans, and animals and ecofriendly approaches such as bioremediation and phytoremediation for degradation and detoxification for environmental safety. For this book, a number of experts from colleges, universities. and research laboratories have contributed their valuable knowledge on the relevant topic, which will be quite useful for readers to get more information on the subject matter. All the chapters compiled in this book cover the different aspects of environmental problems and their remedies with up-to-date developments in the field of biodegradation and bioremediation including the use of various group of microbes for environmental remediation, terrestrial/aquatic plants for phytoremediation of toxic metals from contaminated sites, constructed wetlands for treatment of industrial wastewaters, microbial enzymes for degradation and detoxification of environmental pollutants, biosurfactants for remediation of petroleum hydrocarbons and heavy metals, biodegradation and bioremediation of azo dyes, pesticides, plant–microbe interactions for environmental remediation, and various emerging technologies such as electro-bioremediation, nano-bioremediation, and microbial fuel cell for environmental management.

This book will be of great value to researchers, environmental chemists and scientists, microbiologists and biotechnologists, eco-toxicologists, waste treatment engineers and managers, environmental science managers, administrators and policy makers, industry persons and students at bachelor’s, master’s, and doctoral level in the relevant field. Thus, in this book, readers will find the updated information as well as the future direction for research in the field of environmental management.

Lucknow, India Ram Naresh Bharagava

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The edited book entitled *Emerging Ecofriendly Green Technologies for Wastewater Treatment* is the outcome of long dedicated efforts of many individuals, who directly or indirectly supported me during the compilation and upbringing of this valuable edition; many of whom deserve special mention.

The Editor is highly thankful to all the national and international contributing authors for their valuable submissions, cooperation and providing most up-to-date information on the diverse aspects of the subject regardless of their busy schedules.

I am extremely thankful to our Series Editor, Prof. Naveen Kumar Arora, and Publishing Editor, Ms. Aakanksha Tyagi, for the encouragement, support and valuable advice, and skillful organization and management of the entire book project; Ms. Vaishnavi Venkatesh for moving the book through the production process in an efficient and professional manner.

I am also heartily thankful to the Almighty God for helping me through the entire journey and making the experience enjoyable. Further, we hope that this book will be of great value to researchers working on *Wastewaters and their Treatment* and will go some way to make our planet safe and greener. At the end, we seek to learn more on the subject through the valuable comments, reviews, and suggestions from our readers.

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Chapter 1
Green Technologies for the Treatment of Pharmaceutical Contaminants in Wastewaters

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Abstract The remarkable worldwide increase in the production and use of several pharmaceuticals, on one hand, brings advantages to modern society and, on the other hand, represents a hazardous risk to natural ecosystems. Pharmaceuticals are considered emerging contaminants of great environmental concern since its continuous disposal in the environment and high persistency can affect ecosystems and human life quality. In this context, the scientific community has addressed this problematic in several fronts investigating incidence, toxicological effects, and detection techniques to determine the real impact of the increase of its release as one of the challenges of the new millennia. The present chapter approaches the occurrence, and deleterious effects of these contaminants, as well as the alternative treatments developed to adequately remove them from natural water bodies and water streams.

Keywords Wastewaters · Pharmaceutical contaminants · Hazardous risks · Green technologies · Treatment

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1.1 Introduction

Emerging contaminants have no proper definition, being hard to describe and classify (Tijani et al. 2016). The US Geological Society defines the emerging contaminants as synthetic or naturally occurring chemicals, microorganisms, or metabolites that are not monitored but have the potential to cause adverse ecological and/or human health effects (USGS 2014). Recent research shows that the use of pharmaceuticals will globally reach 4500 billion doses by 2020, approximately 24% more than in 2015; at the same time, 50% of the world population will be able to consume more than one dose per person per day. Compared to consumption, global spending for pharmaceuticals is mostly driven by the USA, EU (Germany, the UK, Italy, France, Spain), Japan, Canada, South Korea, and Australia (QuintilesI MS Health, 2015, 2016), with an overall market of $1400 billion by 2020 (Mezzelani et al. 2018).

The development of analytical techniques such as high-performance liquid chromatography-mass spectrometry (HPLC-MS) allowed the detection of several compounds in complex matrixes identifying and quantifying the compounds in concentrations as low as nanograms per liter. Considering their high toxicity and the ability to move along the food chain, most times even nano-level of contaminations is enough to see deleterious effects promoted from contact with pharmaceuticals (Rivera-Utrilla et al. 2013; Yadav et al. 2016a; Comber et al. 2018). Attempts like the Stockholm Convention, also known as the Persistent Organic Pollutants Treaty of 2001, and the Berlaymont Declaration of 2013 have been made seeking to control the level of these contaminants in the environment, without success.

Among the emerging contaminants, pharmaceuticals are classified according to their uses adding to up to 24 classifications, of which four are predominantly found in water and are known as nonsteroidal anti-inflammatory drugs (NSAIDs), anticonvulsants, antibiotics, and lipid regulators (Tijani et al. 2016). The first reports of pharmaceuticals as environmental contaminants were only found when ethinylestradiol (birth control substance) was directly related to neurological impairment found in fishes back in 1994 (Gautam et al. 2017; Purdom et al. 1994), but their effects on the environmental balance vary from disrupting key bacterial cycles (nitrification/denitrification) to impairments in soil fertility (Watkinson et al. 2009). With the increase in human and animal use of these drugs, and due to the incomplete metabolization of these compounds, an increase in volume detected in the environment has been seen in recent years. Although most of the pharmaceuticals reach the wastewater treatment plants after being somewhat digested by human and animal organisms, there is still a great amount of the contaminants that reach the systems as purchased due to inadequate disposal of these compounds (Pereira et al. 2017).

This problem is accentuated when considering that conventional wastewater treatment plants do not reach complete mineralization of these compounds, which several times exits the system unchanged (Yadav et al. 2016b; Zhang et al. 2018). The scenario is more problematic when considering practices of water reuse, especially adopted in areas where the resource is scarce. For instance, Kleywegt et al.

(2011) detected more than 30 different pharmaceuticals in drinking water across the world.

Endocrine disruption, chronic toxicity, and increase in bacterial strain resistance to these drugs are the main side effects already spread worldwide. Hence, pharmaceuticals and several emerging contaminants are being even more frequently the focus on research and investments in order to better understand their incidence and their fate in natural environments. In this sense, UNESCO-IHP initiative funded by the Swedish International and Developed Cooperation Agency (Sida) just invested in studies in 17 different countries (Australia, Brazil, China, Ethiopia, India, Kenya, Kuwait, Mexico, Mongolia, Nigeria, Norway, Rwanda, Saint Lucia, Thailand, Tunisia, Ukraine, and Vietnam).

Notably, efforts from various entities are starting to promote awareness of the problem and address possible solutions and research on the topic. However, pharmaceutical pollution control protocols involve both political and cultural changes demanding intensive and direct participation of the standard home user. With this background, this chapter presents a critical review of the recent scientific development on the issue of presenting environmentally friendly options for pharmaceutical removal from the environment. In addition, a summary of the main pharmaceuticals found in the environment and the latest detection methods is presented. Finally, the uses of environmentally friendly technologies named green technologies for the elimination of these compounds from the environment are also discussed.

1.2 Occurrence of Pharmaceuticals Worldwide

The presence of pharmaceutical contaminants in the wastewater is directly related to human activity and, as such, is highly unpredictable. Partly, this is because these contaminants can enter the environment from several sources (Fig. 1.1). However, household wastewater is one of the main sources for pharmaceuticals found in the environment (Pereira et al. 2017). Additionally, pharmaceuticals used in veterinary applications are commonly excreted directly into soils or superficial waters without proper treatment, which increases the complexity of emission estimation (Bielen et al. 2017).

Due to their physical-chemical properties, high stability, and chemical persistence, pharmaceuticals are generally hard to naturally degrade. In a more concerning scenario, their chemical structures can present specific affinities that lead them to bond, rearrange, and develop synergistic effects resulting in a more bioactive compound than their metabolic precursor (Luo et al. 2014; Zainith et al. 2019). Various routes by which the pharmaceuticals enter the environment can be seen in Fig. 1.1 (Tijani et al. 2016; Verlicchi et al. 2012; Ding et al. 2010; Yang et al. 2017a; Scott et al. 2018).

Therefore, it is no surprise that pharmaceuticals have been found in both influent and effluent waters from wastewater treatment plants (WWTP) (Comber et al. 2018; Verlicchi et al. 2012; Cotillas et al. 2016; Guedes-alonso et al. 2013), surface water

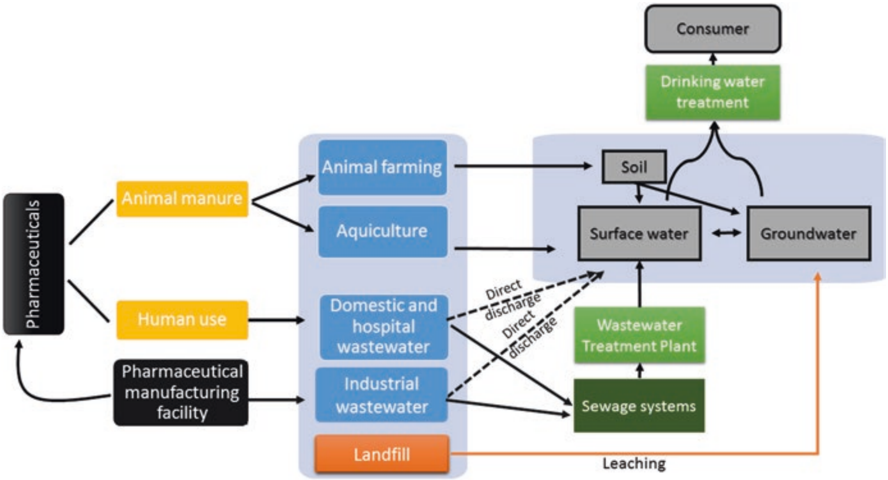

Fig. 1.1 Schematic pathways of pharmaceutical contaminants from sources to receptors (gray) (Adapted from Stuart et al. (2012))

Table 1.1 Pharmaceutical classes and representative compounds intensely consumed worldwide according to its use

Classes	Representative compound
Antibiotic	Erythromycin; sulfamethoxazole
Antimicrobial	Oxytetracycline, trimethoprim
Anti-inflammatory	Acetylsalicylic acid; ibuprofen; diclofenac
Analgesic	Paracetamol
Antidepressants	Benzodiazepines
Antiepileptics	Carbamazepine
Lipid-lowering drugs	Fibrates
β-Blockers	Atenolol, propranolol, and metoprolol
Antiulcer drugs and antihistamines	Ranitidine and famotidine
Other substances	Cocaine, barbiturates, methadone, amphetamines, opiates, heroin, and other narcotics

(Bielen et al. 2017; Marsik et al. 2017; Mandaric et al. 2017), groundwater (Yao et al. 2017; Sui et al. 2015), and even drinking water (Machado et al. 2016; Saxena et al. 2015; Leung et al. 2013; Mompelat et al. 2009). Among the several compounds found in literature, a brief summary of the most frequent classes of pharmaceuticals and representative compounds is displayed in Table 1.1 (Kümmerer 2001; Balakrishna et al. 2017; Puckowski et al. 2016).

In countries like China, known as the largest producer and consumer of pharmaceuticals in the world, amounts of over 90,000 tons of antibiotics were estimated to be consumed, of which 53,800 tons entered the environment through WWTP (Zhang et al. 2018). The loadings vary according to the season, sporadic events, intra- and inter-day variation, and spatial distribution, which all contribute to the difficulty to properly predict the amounts of contaminants found in the environment (Petrie et al. 2014). Further, urban and anthropic variables, such as tourism and collective vacation periods, have been found to significantly alter the incidence of pharmaceuticals in the environment (Mandaric et al. 2017). For example, studies developed by Mandaric et al. (2017), analyzing the incidence of 80 different pharmaceutical compounds in the Adige river basin (Italy), found that the overall presence of the compounds was higher in winter than in summer.

However, considering the distribution throughout over 400 km of the river and 12 different sampling points, it was proven that this difference is related to both the larger dilution seen in summer, due to the snow melting and the higher presence of tourists during winter. Similarly, Azzouz and Ballesteros (2013) and Pereira et al. (2015) analyzed the influence of environmental conditions on the concentration of pharmaceuticals, hormones, and personal care products in samples of raw water received by a WWTP in southeastern Spain. The research focused on determining the presence of compounds most resistant to removal by conventional wastewater treatment. Higher levels of these contaminants were observed in colder periods than in warm periods (spring and summer), which was mainly attributed to the biodegradation being favored by high temperatures and solar irradiance. On the other hand, carbamazepine in raw water presented only little change between periods, which suggests that this pharmaceutical is resistant to changes in temperature and solar irradiance.

Finally, the efficiency with which these contaminants are removed by a conventional water treatment plant operating by means of peroxidation with potassium permanganate and chlorination with sodium hypochlorite in the presence of highly concentrated ammonia was evaluated (Saxena et al. 2015; Bharagava et al. 2018). As result, it was found that water treated in the colder periods still contained small amounts of ibuprofen and carbamazepine (0.09–0.50 ng L^{-1}), these values being less than 0.2% of their initial concentrations at the WWTP intake.

On the other hand, Marsik et al. (2017) analyzed the concentration of five of the most common nonsteroidal anti-inflammatory drugs (NSAIDs) (ibuprofen, diclofenac, naproxen, ketoprofen, and indomethacin) collected in 29 sites, including urban and rural areas, water streams, and main water supply points in the Elba river in Czech Republic. Although the amount of NSAID varied according to the sampling point, in general, their concentrations increase during the months of spring and autumn. In this study, ibuprofen was the most abundant compound found (3.210 ng L^{-1}), followed by naproxen, diclofenac, and ketoprofen (1.4238 ng L^{-1}, 1.080 ng L^{-1}, and 929 ng L^{-1}, respectively). Additionally, factors like flow rates also influenced the concentration of all compounds showing a significant increase in creeks, probably associated with the proximity to the contamination source.

Kot-Wasik et al. (2016) investigated the occurrence and efficiency of removing 25 pharmaceuticals during water and wastewater treatment analyzing the seasonal variation noted throughout the year. The compounds found more frequently were carbamazepine (100% of the samples) and ibuprofen (98% of the samples). Still, pharmaceutical concentrations were higher in winter, especially for the nonsteroidal anti-inflammatory drugs (NSAIDs) and caffeine, probably due to degradation inhibition related to low temperatures and limited sunlight. Carbamazepine was once again found as the most resistant to natural degradation, and its concentration was uniform throughout the year.

Therefore, complex studies like these, which seek to understand the anthropogenic effect on the concentration of pharmaceuticals throughout the year, promote a better knowledge of the various routes in which population density can affect contamination rates and aid in developing adequate protocols to suit various environments. Nowadays, an increasing concern on the presence of these contaminants in drinking water is seen, especially in governmental studies. Kleywegt et al. (2011) reported a survey carried out by the Ontario Ministry of the Environment (MOE), analyzing 258 field samples, collected through the timespan of 16 months. Incidence of pharmaceuticals and other emerging contaminants is widely reported in drinking water samples in this study, highlighting the need for improvements in the treatment used to remove these specific compounds.

Moreover, the amounts in which these compounds are found have become an alarming problem. Kay et al. (2017) analyzed the Aire and Calder catchment in West Yorkshire (UK), which receive 105 WWTP effluents being the most populated area of the UK with close to 1.5 million people. For analysis, only five of the most commonly found compounds were analyzed in the samples gathered, which were 121 WWTP effluents, 185 receiving waters, and 14 combined sewer outflows. The compounds analyzed were diclofenac, erythromycin, ibuprofen, mefenamic acid, and propranolol. After thorough analysis, the pharmaceuticals chosen were found in 51–94% of the samples in concentrations up to tens of hundreds of ng L^{-1}, many times exceeding the permissible values found in legislation. Although the variety of products found in effluents and surface waters is endless, studies can have a range as wide as hundreds of compounds and still not effectively characterize all the compounds found in samples collected. Worldwide the number of contaminants identified in these studies is continuously increasing. Table 1.2 shows the latest studies highlighting the analysis method applied and the water matrix chosen in each case.

When brought to light, the incidence in which contaminants are found in natural water bodies only reinforces the need to improve the WWTP. Studies developed in South Korea frequently detected incomplete removal of 25 compounds from the total of 26 analyzed by the WWTP, even in systems relying on membrane filtration, membrane bioreactor, nanofiltration, reverse osmosis, and ultraviolet irradiation (Kim et al. 2018; Chowdhary et al. 2018). Further, this situation is even more worrisome in countries with poor environmental protection laws. In such places, the contamination occurs notably by poor understanding from the population, disposing pharmaceuticals directly into toilets and water bodies, combined with limited contamination control measurement adopted by hospitals, treatment centers, and even industries (Visanji et al. 2018).

In countries like India, fiscal incentives and low employee costs will drive the pharmaceutical industry to produce $45 billion a year by 2020, where sewage treatment is so deficient that from 1.3 billion people attended, only 31% of the sewage

Table 1.2 Reports on pharmaceutical compounds found in natural waters worldwide

Country	Number of contaminants identified	Environment analyzed	Analysis method	Year	References
South Korea	26	Effluents, surface waters, drinking water	LC-MS/MS	2007	Kim et al. (2007)
Canada	48	Surface waters, drinking water	Q-trap MS LC-MS/MS	2011	Kleywegt et al. (2011)
Australia	28	Hospital wastewaters, WWTP effluent, surface waters, drinking waters	HPLC-MS/MS	2006	Watkinson et al. (2009)
Italy	80	Surface waters	UPLC-QLIT-MS^2	2017	Mandaric et al. (2017)
China	14	Ground water and surface water	HPLC-MS/MS	2017	Yao et al. (2017)
Spain	13	Wastewater	HPLC-MS/MS and UHPLC-MS/MS	2013	Guedes-alonso et al. (2013)
Spain	23	WWTP	LC-MS/MS	2017	Afonso-Olivares et al. (2017)
Spain	19	Wastewater	UPLC-Qtrap-MS	2017	Hom-Diaz et al. (2017)
India	67	Wastewater, hospital effluent, river water, ground water		2017	Balakrishna et al. (2017)
China	37	WWTP	HPLC-MS	2018	Zhang et al. (2018)
China	39	Advanced drinking water treatment plant	HPLC-MS/MS and LC/MS/MS	2016	Lin et al. (2016)
South Africa	90	WWTP, surface waters	UPLC-TQD-MS	2017	Archer et al. (2017)
Kenya	21	Rivers	UPLC	2018	K'oreje et al. (2018)

(38.254 million liters per day) is actually treated (Balakrishna et al. 2017). Although proper treatment methods and adequate environmental policies are still in development in these countries, an increase in studies focusing on the detection and quantification of pharmaceuticals in the environment has been noted (Gogoi et al. 2018).

Yao et al. (2017) investigated the occurrence of 14 antibiotics (fluoroquinolones, tetracyclines, macrolides, and sulfonamides) in groundwater and water bodies in the fields of Jianghan in China, during three seasons. Total concentrations of target compounds in water samples were higher in spring than in summer and winter, mostly associated with veterinary use and the higher incidence of diseases in this period. Erythromycin was the antibiotic found mostly in superficial waters with an average concentration of 1.60 μg L^{-1}, 0.772 μg L^{-1}, and 0.546 μg L^{-1}, respectively, in spring, summer, and winter.

Matongo et al. (2015) investigated the presence of pharmaceuticals, such as sulfamethazine, sulfamethoxazole, erythromycin, metronidazole, trimethoprim, acetaminophen, caffeine, carbamazepine, clozapine, and ibuprofen in the Umgeni River, in the Durban city in KwaZulu-Natal, South Africa. Clozapine was found in higher concentrations (78.33 μg L^{-1}) followed by ibuprofen (62.0 μg L^{-1}).

Machado et al. (2016) investigated the presence of emerging contaminants of different classes in 100 samples of potable water in 22 Brazilian capitals, and seven water sources from most populated areas in the country. The samples were collected between June and September of 2011 and again in the same period of 2012. Among the emerging contaminants, caffeine was the substance most commonly found, detected in 93% of the potable water samples, and in 100% of the surface waters. Caffeine concentration in potable water varied from 1.8 ng L^{-1} to 2 μg L^{-1}, while in water sources, the concentrations varied from 40 ng L^{-1} to about 19 μg L^{-1}. The fact that caffeine is found in potable water indicates that there is still reminiscent of domestic wastewater contamination in potable water distribution since this is typically an anthropogenic compound. Similar results were found in studies carried out in China (Leung et al. 2013) and Spain (Boleda et al. 2011).

On the other hand, Watkinson et al. (2009) analyzed the presence of 28 antibiotics in hospital wastewaters, WWTP effluent, surface waters, and drinking waters and found that although the presence of antibiotics was seen in every sample, including surface water used as drinking water extraction sites, none of the antibiotics analyzed were found in drinking water samples. Thus, the samples collected from 81 different surface water and 20 different drinking water sites within South-East Queensland (Australia) pointed out that the treatment applied to the drinking water supplied to the population was satisfactory for antibiotic removal, which represents hopes in developing adequate treatment and distribution protocol for the critical areas.

The most delicate part of these studies relies on identifying adequately the presence of the compounds on the intake and output of the WWTP. In this sense, an innovative research developed by Sgroi et al. (2017) used fluorescence data of three-dimensional excitation—emission matrixes (EEM) to analyze treatment efficiency of 10 WWTP facilities in Sicily (Italy) using 11 target compounds. These WWTP presented secondary treatments varying from activated sludge units with nitrification and denitrification processes, activated sludge units without nitrification and rotating biological contactors, or even extended aeration activated sludge unit (Kumari et al. 2016; Saxena et al. 2017). All compounds were removed in a range from 28 to 82%; however, due to treatment efficiencies varying among the WWTPs proposed, the development of rapid, low-cost, and highly specific studies like these enable the tailoring of systems more adequately addressing the influent for every matrix it presents.

Finally, all the studies mentioned contamination found in untreated wastewater and/or the persistent contamination found after the effluent exits the WWTP. However, considering that, for example, one in four households in the United States relies on septic systems for wastewater disposal, further investigation on the direct influence of this route is also necessary. Yang et al. (2017b) studied the fate of pharmaceuticals in septic systems considering drain fields of drip dispersal, gravel trench, and advanced system. Although the septic systems can treat partially the compounds analyzed, it also serves as an accumulation point for their byproducts. Additionally, these accumulation points infiltrate to groundwater contaminating the water source, which was confirmed in this study by identifying seven markers directly below the septic systems studied.

1.3 Ecotoxicological Effects

Other than toxicological effects related to direct exposure to pharmaceuticals, a concerning process occurring is the increase in microbial resistance normally caused by interaction with human and animal bacterial species, exposure to bacteria present in hospital, farms and home care, and finally interaction with bacteria present in sewage and biological wastes (Mishra and Bharagava 2016; Pereira et al. 2017; Gavrilescu et al. 2015).

Analyzing pharmaceutical ecotoxicological effect is normally carried out in laboratorial environment based on acute toxicity tests to a certain compound. The most commonly used organisms are fishes *Danio rerio* and *Pimephales promelas* and the crustaceous *Daphnia magna*, using standard methods measuring the concentrations that cause oxidative stress and/or mortality to the organism tested. One of the most common methods used is the effect concentration 50% (EC_{50}), which determines the concentration in which adverse effect is noted in 50% of the individuals (Petrie et al. 2014; Galus et al. 2013). Therefore, a compound is considered harmful when its EC_{50} is between 10 and 100 mg L^{-1}, toxic at 1–10 g L^{-1}, and highly toxic when <1 mg L^{-1} (Petrie et al. 2014). However, data comparison in literature is very complicated due to the specific compounds and species tested, as well as the variety of toxicological endpoints studied. Table 1.3 shows the EC_{50} found for a group of compounds tested using organisms *D. magna, V. fischeri, A. flos-aque, P. subcapitata, S. vacuolatus, and S. obliquus*.

Various factors affect the toxicity of certain compounds, and due to the sensitive nature of the species analyzed, variables such as temperature, pH, salinity, and turbidity, need to be considered as well (Yadav et al. 2019; Mani and Bharagava 2016). Mostly, for pharmaceutical contamination, the main factor affected is the pH of the water bodies. Recent studies by Liu et al. (2016) analyzed the toxicity of sulfadiazine to *Daphnia magna*, in various pH presenting toxicity increments up to 15-folds in EC50, when pH reduced from 8.5 to 6.0. Similar results had been previously reported by Anskjær et al. (2013), finding 11-fold increment in EC50 with the same pH variation, relating the specific transformation from its neutral form at pH 6.0 to its negatively charged form at pH 8.5.

Table 1.3 Estimations of the effective concentration (EC_{50}) for several organisms exposed to a variety of pharmaceutical compounds

Compound tested	Organism tested	Endpoint	Toxicity (mg L^{-1})	References
Sulfadiazine	*D. magna*	24 h EC_{50}	48.89	Liu et al. (2016)
		48 h EC_{50}	11.93	
Diclofenac	*D. magna*	24 h EC_{50}	3.18	Czech et al. (2014)
	V. fischeri	48 h EC_{50}	2.69	
	D. magna	14.04	14.04	
Chloramphenicol	*V. fischeri*	24 h EC_{50}	5	
	D. magna	48 h EC_{50}	5	
		27.06	27.06	
Metoprolol	*V. fischeri*	24 h EC_{50}	2.59	
		48 h EC_{50}	2.59	
		14.48	14.48	
Oxytetracycline	*Anabaena flos-aque*	72 h ErC_{50}	2.7	Kolar et al. (2014)
	Pseudokirchneriella subcapitata	72 h ErC_{10}	1.5	
	Daphnia magna	72 h ErC_{50}	1.04	
		72 h ErC_{10}	0.47	
Trimethoprim	*Anabaena flos-aque*	48 h EC_{50}	669[a]	
	Pseudokirchneriella subcapitata	48 h EC_{10}	197	
	Daphnia magna	72 h ErC_{50}	253	
		72 h ErC_{10}	26	
		72 h ErC_{50}	129	
		72 h ErC_{10}	65	
		48 h EC_{50}	100	
		48 h EC_{10}	66	

(continued)

Table 1.3 (continued)

Compound tested	Organism tested	Endpoint	Toxicity (mg L^{-1})	References
Sulfamethoxazole + sulfamethazine	*Scenedesmus vacuolatus*	72 h EC_{50}	19.52	Xiong et al. (2018)
	Scenedesmus obliquus	96 h EC_{50}	0.108	
Diclofenac	*D. magna*	24 h EC_{50}	82.3	Du et al. (2016)
		48 h EC_{50}	18.1	
		72 h EC_{50}	6.23	
Ibuprofen	*D. magna*	24 h EC_{50}	116	
		48 h EC_{50}	23.5	
		72 h EC_{50}	8.33	

[a]Value exceeded water solubility

Additionally, it is common to find that the by-product formed after degradation of the original pharmaceutical is many times more toxic for the studied organism than its previous form. For example, Dirany et al. (2012) analyzed the degradation of sulfachloropyridazine by electro-Fenton treatment and further analyzed the toxicity of the target compound and two of its oxidation by-products, namely amino-6-chloropyridazine and *p*-benzoquinone. Analyzing the toxicity in *V. fischeri*, they found EC_{50} of 1.96 mg L^{-1} for sulfachloropyridazine and <0.01 mg L^{-1} for *p*-benzoquinone and over 250 mg L^{-1} for 6-chloropyridazine. Considering the degradation chain follows the sequence sulfachloropyridazine > 6-chloropyridazine > *p*-benzoquinone, a sharp increase in toxicity is seen in an intermediary step of the treatment, which is a common finding when treating pharmaceuticals (Coledam et al. 2017).

Nevertheless, study on bioaccumulation of pharmaceuticals and their effects on the health of the species exposed to them is still a field to be widely researched. Cheng et al. (2017) reported the bioaccumulation of sulfadiazine in Chinese mitten crab (*E. sinensis*), finding rates of <3 ng/g, not dose-dependent. These researches increase the understanding of the secondary effects promoted by the environmental contamination of these compounds and aid in the development of new treatment protocols and risk identification.

Another particularly interesting study was developed by Mohd Zanuri et al. (2017) analyzing the effects of short-term exposure to realistic values of ibuprofen, diclofenac, and sildenafil citrate of selected specimens: echinoderms (*Asterias rubens* and *Psammechinus miliaris*) and a polychaete worm *Arenicola marina*. From the compounds analyzed, diclofenac was more toxic than the others reducing sperm swimming speed and fertilization success in *A. rubens*. Exposure to sildenafil citrate (commercially known as Viagra®) actually enhanced sperm motility, which increased fertilization success in the echinoderms, which also did not present toxicity effects for this organism. Case studies like these are important to highlight the various toxic effects possible in environmental conditions.

Additionally, one of the main problems in estimating the toxicity of real effluents is that in many processes and in urban scenarios, the organisms are exposed to a complex mixture of compounds, and it is difficult to estimate EC_{50} for the compounds found. For example, Bielen et al. (2017) studied the effluents from two pharmaceutical companies in Croatia, collecting samples in four different periods throughout the year, analyzing seasonal effects. Sample one contained mostly azithromycin and erythromycin, while sample two contained sulfonamides, fluoroquinolones, tetracyclines, and β-lactams. *D. rerio* specimens were exposed to the effluent as in loco (after undergoing a membrane reactor treatment) and 2× diluted and 4× diluted. Mortality rates for the effluent from Company 1 as in loco were 100%, showing improvement to as low as 20% only after a 4× dilution. Meanwhile, the specimens exposed to effluent from Company 2 varied from under 10% mortality to no mortality after dilution. Studies like these highlight the complexity of ecotoxicity tests in case of pharmaceutical contamination supporting the need for Predicted No Effect Concentrations (PNECs) for all compounds being emitted in the environment.

1.4 Alternative Treatments

1.4.1 Microalgal

Studies developed in Spain by Hom-Diaz et al. (2017) analyzed the effectiveness of a tubular microalgae reactor for toilet wastewater treatment system for pharmaceutical removal. The system consisted of 1200 L microtubular tanks and a constant stirring velocity of 0.13 m s^{-1}, analyzing the system efficiency in two periods of the year (period 1: September 14 to October 16; period 2: October 20 to December 22), in order to analyze both seasonal effects and possible variations in population's consumption of pharmaceuticals. These studies also analyzed two hydraulic retention times of 8 and 12 days. In general, the system was able to remove 98% of the anti-inflammatory drugs, 48% of antibiotics, and between 30 and 57% of the psychiatric drugs, proving effectiveness for this proposed system to remove pharmaceuticals present in natural wastewaters.

Furthermore, extensive research has been carried out by Xiong et al. (2018) gathering the latest studies on microalgae used to remove pharmaceuticals from water sources in microalgae-mediated bioremediation, highlighting the possibility of solar energy use, eco-friendliness, and its low cost. The research classified microalgae treatment in bioadsorption, bioaccumulation, and biodegradation. Bioadsorption is highly recommended for pharmaceuticals with cationic groups that are actively attracted to the microalgae surface due to electrostatic interaction. Bioaccumulation that is the uptake of substrates has been proven successful with specific pharmaceuticals like carbamazepine (Xiong et al. 2016). Finally, biodegradation was found to be the most common route for pharmaceutical removal by microalgae treatment, finding removal rates of up to 80% of active compounds according to the literature (Xiong et al. 2018).

When considering microalgae removal rates, a series of factors come into play, as seen in recent studies developed by Xiong et al. (2019), where sulfamethoxazole and sulfamethazine were combined at various concentrations and submitted to microalgae degradation with *S. obliquus*. While seeking to understand the degradation route of the compounds studied, it was possible to note that the degradation of sulfamethazine was considerably improved with the addition of sulfamethoxazole. By determining the degradation routes present, it was confirmed that *S. obliquus* was able to promote hydroxylation, methylation, deamination, and bond cleavage, all of which could contribute to the understanding and determination of the potential applications of this specific organism.

Microalgae is, therefore, one of the proposed solutions for pharmaceuticals removal from water bodies and various wastewaters. Mostly, the recent trends involve combined processes where the system is optimized by a previous or posterior microalgae treatment. In this sense, studies on integrating microalgae with advanced oxidation processes (AOPS) (Keen et al. 2012), constructed wetlands (Ding et al. 2016), and microbial fuel cells (Li et al. 2014) are being performed.

1.4.2 Advanced Oxidation Processes (AOP)

Contamination with certain pharmaceuticals due to their specific properties and high stability are typically hard to address. In this sense, the AOPs are known to be an effective indiscriminate method to strongly oxidase the most organic compounds. Furthermore, even in cases where the target compound is not totally degraded, the addition of hydroxyl groups to the parent molecule facilitates ring opening by certain catechol dioxygenase enzymes produced by heterotrophic bacteria being a critical step in biotransformation of aromatic compounds (Keen et al. 2012).

Ozonation, UV, photocatalysis, and Fenton reaction have been used for the treatment of potable water and to a lesser extent in wastewater disinfection. It has been reported that WWTPs equipped with AOPs were capable of eliminating pharmaceutical compounds, such as caffeine and sulfamethoxazole, at efficiencies of 89.5% and 92.2%, respectively (Lin et al. 2016).

Among the AOPs available, UV treatment is used as one of the main disinfection techniques in European Wastewater Treatment Plants considering its high disinfection capacity with no addition of chemicals required (Song et al. 2016). In a sense, the treatment efficiencies in WWTP have not been thoroughly addressed due to variations in environmental concentrations and specific operatiing conditions that are typically difficult to simulate in lab-scale reactors. However, Paredes et al. (2018) researched the fate of 12 different pharmaceuticals, analyzing UV dose, temperature, and water matrix in order to determine the real applicability of the UV treatment. The effluents tested were collected from four different WWTP in Spain, UV dose varied from 12 to 44 mJ/cm^2, and contaminant concentration was spiked at environmentally relevant concentrations (10 μg L^{-1}). Phototransformation was seen in most compounds in rates varying from 60 to 92%, with a considerable increase in degradation when the temperature was altered from 15 to 25 °C.

Although Paredes et al. (2018) found high rates of degradation for recalcitrant compounds (such as diclofenac and diazepam), the phototransformation of the pharmaceuticals in full-scale system is almost negligible due to the low doses of UV applied in the system, also impaired by variables such as total suspended solids, dissolved organic matter, and nitrate concentration. These results suggest that the UV method, once it is present in most WWTP as a disinfection procedure, could be a viable route to improve the removal rates of pharmaceuticals if combined with catalytical processes.

In this sense, Keen et al. (2012) analyzed the degradation of carbamazepine, a well-known and very persistent drug prescribed for epilepsy and other mental disorders, by combining UV/H_2O_2 and biodegradation. Their study determined that the initial UV/H_2O_2 attacking the compound with the hydroxyls formed and leading to the formation of assimilable organic carbon (AOC) enables the biofilm growth. Additionally, the UV/H_2O_2 coupled with a traditional WWTP could also provide higher levels of disinfection, possibly even removing the need for that additional final step from the process.

1.4.3 Adsorption

Basically, considering a physical treatment approach, adsorption is well known for being highly efficient, low cost, and easy operation and presents no risk of formation of toxic products. It can be applied as a batch process or in the form of fixed-bed columns that is easily scaled up (Ahmed and Hameed 2018).

Improvements in the physical structures of adsorbents are another approach to increase their effectiveness when treating effluents contaminated with pharmaceuticals. In that sense, Shan et al. (2017) supported graphene oxide (compound widely known for its adsorptive features) onto rigid fluorine-containing molecules (TFT or DFB) analyzing its capacity to adsorb carbamazepine, sulfamethoxazole, sulfadiazine, ibuprofen, paracetamol, and phenacetin solutions. The enhancements proposed by doping the graphene oxide on the DFB structure can increase the adsorption capacity by 1.0–15 times, highlighting the potential for the use of this technology efficiently adsorbing these molecules from water bodies.

Further, since adsorption is mostly dependent on particle size, other improvements can be done to enhance the adsorption rates, especially when treating nanoparticles. In this sense, procedures such as coagulation would ensure the separation of larger particles allowing the use of filtration systems with smaller pores. Thus, Sheng et al. (2016) combined an ultrafiltration system with coagulation and powdered activated carbon pretreatment to address samples containing acetaminophen, bezafibrate, caffeine, carbamazepine, cotinine, diclofenac, gemfibrozil, ibuprofen, metoprolol, naproxen, sulfadimethoxine, sulfamethazine, sulfamethoxazole, sulfathiazole, triclosan, and trimethoprim. By developing this procedure, they noted that pharmaceuticals would bond to the activated carbon by weak Van der Walls attraction forces, which would be retained in the ultrafiltration system blocking the passage of further pharmaceuticals.

Sheng et al. (2016) studied the effects of coagulation, activated carbon, and ultrafiltration alone and combined, finding that for the individual technologies, rates of 50, 29, and 7% removal were found for the activated carbon, ultrafiltration, and coagulation alone, respectively. As for the proposed combined process of ultrafiltration with coagulation pretreatment showed an improvement of only 4% in removal rates. Finally, rates of 90.3% removal were found when combining ultrafiltration with activated carbon use.

When focusing on adsorption using activated carbon, researchers have found good removal rates, but due to the high cost of activated carbon, the reuse of these materials is of great concern. In this sense, Marques et al. (2017) analyzed the thermal regeneration of activated carbon in granular, powdered, and cloth forms studying the retention of chlorofibric acid and paracetamol. The materials were tested for absorption capacity and then submitted to thermal regeneration in 400 and 600 °C. The procedure was repeated after every adsorption experiment for four cycles. Among the materials tested, carbon felt presented the highest regeneration capacity maintaining its activity over 50% up to the second reuse, decreasing to fewer than 20% at the fourth reuse in both the temperature conditions. Although the results in these tests are interesting, the need to develop efficient recovering systems is one of the main limiting factors for the industrial application of adsorption as a route for pharmaceutical removal from effluents.

1.4.4 Enzymatic Bioreactor

Based on the enzymatic capacity to degrade certain chemicals, enzymatic bioreactors are controlled by pH, temperature, and enzyme innate features. Enzymes such as laccases are well known for degrading a wide variety of compounds and their ability to sustain drastic changes in pH. Taking into account the advantages of this degradation route, Asif et al. (2017) proposed the integration of laccase-based bioreactor with high retention membranes coupling the two systems and working with *Aspergillus oryzae (A. oryzae)* and *Trametes versicolor (T. versicolor)*, analyzing degradation and retention of sulfamethoxazole, carbamazepine, diclofenac, oxybenzone, and a pesticide (atrazine). Since degradation by laccase occurs due to the nature of functional groups present in the compounds (e.g., electron-donating capacities) and the relative redox potential of the laccase and the compounds, the findings were particularly analyzed for each compound studied. Considering the combined treatment of membrane filtering and the enzymatic attack by the laccase use, all compounds were removed in rates varying from 50 to 100%.

Likewise, Ba et al. (2018) studied the efficiency of a hybrid bioreactor (HBR) of a combined cross-linked tyrosinase and laccase aggregates and hollow fiber microfiltration (MF) membrane to remove a mixture of 14 pharmaceuticals from municipal wastewater in concentrations at 10 μg L^{-1}. They reported that after a 5-day continuous operation, the HBR achieved >90% efficiency for the elimination of the 14 selected pharmaceuticals at environmental concentration. This outstanding result was attributed to a synergistic action between insolubilized enzymes and membranes. Moreover, the biocatalyst retained nearly 70% of its initial enzymatic activity over the treatment period. In this sense, HBR was proven as an adequate method to treat these compounds inviting the scientific community to further investigate its applicability for the continuous treatment of wastewater.

1.5 Conclusion

To date, discussions on the environmental and human risk of exposure to pharmaceutical contaminants are still in serious debate. It is safe to say that although many studies developing toxicity tests have proven that many pharmaceuticals in low concentration do not impose a risk for human health, in long-term exposure the effective risk of these compounds is still to be properly assessed. Finally, as our understanding of pharmaceutical contamination increases, it becomes clear that certain measurements should be considered. First, the parent compounds are found in the environment mostly due to inadequate disposal of the products; however, their metabolites occur as a natural process of the incomplete consumption by the organism and are frequently as physiologically active as their parent compound. Therefore, special attention should be given to these compounds as well focusing on applying for the advances in wastewater treatment to ensure environmental safety for the following years as the use of pharmaceuticals increases.

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Chapter 2
Constructed Wetlands: An Emerging Green Technology for the Treatment of Industrial Wastewaters

M. Dinesh Kumar, S. Gopikumar, Do Khac Uan, S. Adishkumar, and J. Rajesh Banu

Abstract Constructed wetland treatment methods have been evolved as a consistent treatment technology treating domestic, industrial and agricultural wastewaters. Special attention has been focused on landfill leachate and storm water runoff. Natural wetlands in general remove pollution, but in CWs the conditions are properly monitored, as a result the efficiency in pollution removal is drastic. Removal of the organics and suspended impurities improves the treatment efficiency. Introducing special media for the absorption of nitrogen and phosphorous is focused for removal, which are available in abundant and observed to be the major pollutant. The cost for operation and maintenance of CWs are lower as it requires very less power consumption compared with conventional treatment systems. In addition the design is framed in such a way that it is involved in maintaining the environment during floods and provides habitat for wildlife through dual or multipurpose ecosystems.

Keywords Industries · Wastewaters · Treatment · Constructed wetlands · Green technology

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2.1 Introduction

Insufficient availability of fresh water and poor sanitation are the major problems outbursting in the urbanized world and is observed to be continuing so far; therefore, a proper technology should be adopted. According to WHO and UNICEF report 2017, worldwide 3 out of 10 people are in need of access to fresh drinking water, and every 6 out of 10 are deficient of secure sanitation The increase in water demand is currently being managed by groundwater utility, which is easily available in all geographical areas, though it has been technologically overexploited in all the developing countries (Jiang 2009). Administration of wastewater has been monitored by constructing wastewater treatment plants, but most of the developing countries are giving less priority in treating wastewater (Konnerup et al. 2011; Bharagava et al. 2017; Chowdhary et al. 2017). The outcome of this strategy leads to disposal of untreated wastewater in open streams and lakes (Senzia et al. 2003).

Constructed wetland is considered as potential ecofriendly technology to overcome several environmental issues. This will enhance the wastewater treatment in an innovative, sustainable and cost-effective emerging solution for the environmental protection and restoration (Vymazal 2011a). Natural wetlands have been referred as earth kidneys because they provide the function such as filtering pollutants and nutrients from water that flows through them. Natural wetlands are not to manage wastewater. However, their potential for treating pollutants makes significance in the area of wastewater treatment system. An engineered constructed system imitates the natural wetland functions. This system of treatment unit is intended to progress such as filtration, adsorption, biodegradation, phytoremediation, photo remediation and bioaccumulation with the help of vegetation, soil and microbes for treating wastewater (Chowdhary et al. 2017; Yadav et al. 2017; Mishra et al. 2018).

Conventional system is in regular practice for the treatment of wastewater, but constructed wetlands—the engineered, multidimensional treatment modules which include the unit operation and process—are also observed to be the substitute. The accomplishment is accompanied due to frequent increase in circulation of water, great prospective in water, nutrient reuse, less utilization of energy, less maintenance and effective removal of pollutants (Kadlec and Wallace 2008; Vymazal 2011a; Mishra et al. 2019). The application of this technology in the field of pharmaceutical and personal care products receives wide appreciation by removing the organic and solids contaminant along with toxin metals, nutrients and pathogens (Gikas et al. 2013; Zhang et al. 2014; Yadav et al. 2016a).

The success rate in adopting this technology is due to design and operational variables; its application receives wide appreciation in the field of domestic sewage treatment (Mburu et al. 2013a, b), hospital wastewater (Shrestha et al. 2001), industrial wastewater (Maine et al. 2007; Yadav et al. 2019), agricultural wastewater (He et al. 2006), agricultural runoff (Yang et al. 2008), lake/river water (Li et al. 2009), sludge effluent (Ahmed et al. 2008; Kumari et al. 2016), oil produced wastewater (Ji et al. 2007), storm water runoff (Ávila et al. 2013), sugar factory wastewater (Bojcevska and Tonderski 2007; Bharagava and Chandra 2010), laboratory wastewater (Meutia 2001) and landfill leachate (Nahlik and Mitsch 2006). Phenol removal was the first research work carried out in 1950s in Germany on CWs treating wastewater (Seidel 1961). Meanwhile in the last two or three decades, industrial and agricultural wastewater along with storm water runoff is treated in CWs (Vymazal 2011a).

CW treatment efficiency proves that warm tropical and subtropical climates are essential for treating wastewater (Kivaisi 2001), this is due to exposed sunlight, and have higher microbial action that benefits plant growth round the year, which decrease the time necessary for microbial biodegradation (Zhang et al. 2012). To achieve successful wastewater treatment with CWs, the designs are based on engineered systems that make the most of the usual progression connecting the lowland plant life, earth that is in connection with microbiological throng (Vymazal 2014). Development of treatment capability and to highlight the exact characteristics of wetland ecosystems, the man-made modern treatment wetlands are designed (Kadlec and Wallace 2008). In addition to wetland treatment methods, the advanced constructed wetland treatment is capable of covering a wide variety of priorities that focus on improving the biodiversity and environmental conditions associated with recovering river water quality, accompanying wildlife usage and irrigation of agricultural lands. In connection with treatment terminology, some confusing names have been mentioned such as bio filters, sand filters and green filters.

The CWs are extensive technologies that evolved with time and applications of the hour without the contribution of energy and are the cost-effective and eco-friendly expertise, which supports in removal of pollutants naturally from the wastewater. CWs have some advantages compared to other treatment systems, such as less expensive, natural process, simple construction, less operation and maintenance, stability and cost-effectiveness.

2.2 Current Scenario About Constructed Wetland Treating Industrial Wastewater

This technology deals with minimum energy consumption, using reuse/recyclable materials with renewable sources, without the utilization of chemicals. The effect of a good technology lies in the viability of economical factors protecting the environment with a good acceptance by the community. In treating industrial wastewater, sustainable treatment system associate with the economic growth, environmental and ecosystem protection and public health. CW system can bring the best sustainable treatment to the industries. CWs are known as low-cost and environment friendly engineered system that use vegetation, soil material and microorganism to treat municipal and industrial wastewaters (Nikolaou and Stefanakis 2018). Current studies have focused on exploiting this type of treatment, as it is a better treatment system financially compared with conventional wastewater treatment system.

Normally, the conventional treatments such as activated sludge treatment, trickling filter and anaerobic digestion require more cost investments for their infrastructures. Stefanakis et al. (2014) discussed that the current system of CW gives an efficient method in treating domestic and industrial wastewaters resulting in good effluent quality. These treatments mainly depend on the action of wetland vegetation, microbes and supporting materials. Processes such as adsorption, infiltration and biological degradation are the treatment processes that takes place through vegetation in wetlands (Vymazal 2005). CW is a phytoremediation process that improves the treatment of industrial wastewater (Riggio et al. 2018; Saxena et al. 2019). Phytoremediation is a plant-based significant treatment process in CW to remove pollutants such as organic or inorganic materials and nutrients (Herath and Vithanage 2015; Yadav et al. 2016b). The processes involved in phytoremediation are phytoextraction, phytodegradation, phytostimulation, phytostabilization, rhizofiltration and phytovolatilization (Fig. 2.1).

In phytoextraction, wetland plants absorb the heavy metal through roots from the substance while in phytodegradation, plants accomplished enzymatic breakdown of organic to simpler components either alone or with the help of microbes. Plants in wetland absorb organic materials through roots and release it into atmosphere through transpiration, known as phytovolatilization. Through phytostabilization, plants immobilize the pollutants to diminish the exposure in wetlands. Through phytoremediation, vegetation in CWs enable major mechanisms to remove noxious waste. Thus, treating industrial wastewater in wetland is more economic and environmentally healthy process.

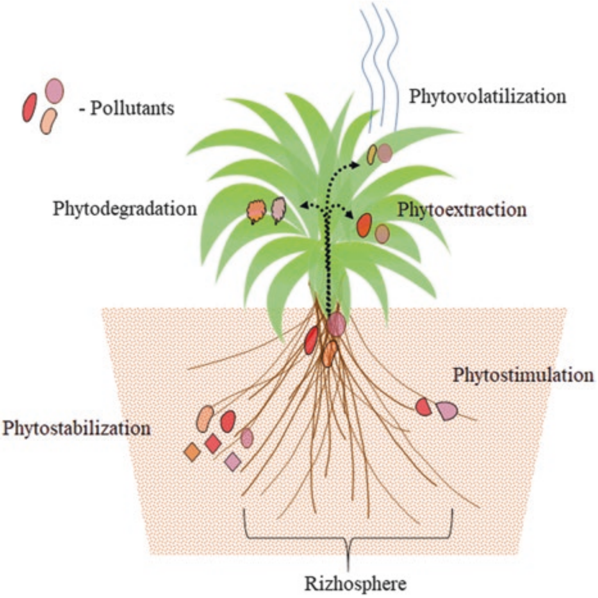

Fig. 2.1 Phytoremediation treatment process in constructed wetland

Stefanakis (2018) reported about a free-flow CW system which treating wastewater from oilfields make available of good occupancy for all birds. This shows that CW systems provide a good ecological system by promoting biodiversity. To improve the treatment efficiency, integrated wetland system was developed. Wu (2008) discussed about the integrated vertical flow constructed wetland (IVCW) that merged with an up flow followed by down flow connected in series. Tao et al. (2010) reported that IVCWs are favourable for anammox process. Saeed et al. (2012) reported about a horizontal subsurface flow CW (HSSCW) system made up of different media such as organic pea gravel, cupola slag and organic coco-peat. Saeed and Sun (2013) used sugar bagasse as supporting media in vertical flow stage of hybrid CW (HCW) which supports nitrogen removal and organic removal from textile wastewater. This is due to the greater porosity and organic carbon leaching action of sugar bagasse. The authors also found out that decolourizing is efficient when they use sylhet sand as media in horizontal flow stage of same HCW.

Pretreatment of domestic and dairy wastewater in a proportion is carried out in Imhoff tank which is further subjected to treatment in a two-stage HSSCW-based CW system connected in series and observed 94% output removal efficiency (Mantovi et al. 2003). Single-stage vertical flow-based CW systems followed by Van Oirschot (2015) deal with the treatment of dairy effluent for the past 16 years and observed significant removal of phosphorus and nitrogen along with organic compounds. Low greenhouse gas emissions compared to other conventional methods while treating the wastewater is an advantage for CW treatment system. In various CW types, surface flow CW (SCW) system produce low CO_2 emissions while VSSCW produces lowest CH_4 emissions, while significant N_2O emissions were produced (Mander et al. 2014).

However, HCW systems attain high removal efficiency with low greenhouse gas emission. MFC is an emerging technology treating the wastewater along with power production (Jayashree et al. 2014, 2016). It has an advantage of less sludge production (Tamilarasan et al. 2018; Kumar et al. 2018). A new approach of integrating CW incorporating microbial fuel cell (MFC) in treating industrial wastewater was introduced. Yadav et al. (2012) demonstrated an integrated CW with MFC treating dye wastewater which results in removal efficiency of 75% with the generation of power density in the range of 15.73 m Wm^{-2}. Presence of both the anaerobic and aerobic circumstances in the process will normally develop the in situ CW-MFC (Yadav et al. 2018). This combined system may offer further electron acceptors that favours the anaerobic zone in the system and improve more power production. New operational approaches are needed to enhance the organic removal and other useful end product such as electricity by treating various industrial wastewaters in CW system.

2.3 Constructed Wetland Classifications

Constructed wetlands (CW) are mainly classified into three systems: (a) surface water flow CW (free water flow) (SCW), (b) subsurface water flow CW (SSCW) and (c) hybrid CW (HCW). In which, first two classifications mainly depend upon their hydrological structure, and the third system is a combination of various CW types. The subsurface water flow also classifies the wetland into two: vertical subsurface water flow CW (VSSCW) and horizontal subsurface water flow CW (HSSCW). Table 2.1 shows the classifications of constructed wetlands.

2.3.1 Surface Water Flow CW (SCW)

SCW are generally a shallow water flow channels or basins with some vegetation which is planted on soil layer (Vymazal 2014). In SCW, water flows horizontally at minimum velocity, forming a water column depth up to 80 cm. This type of CWs is exposed to atmosphere and partially to the sunlight. The wastewater flows through wetland and comes into contact with the vegetation and efficiently removes the pollutants through various physicochemical or biological processes (Wang et al. 2017). Due to the atmospheric diffusion, the upper surface of the wetlands acts as aerobic zones, while the anoxic and anaerobic zones are present nearby the residues. But in high-loading SCW, the anoxic zone is present near the water surface. This type of CWs is used as an advanced wastewater treatment followed by secondary or tertiary treatment. Nitrogen is most effectively removed in SCW by nitrification/denitrification process. Figure 2.2 indicates the schematic representation of surface flow constructed wetland (SCW).

In SCW, nitrifying microbes in aerobic region oxidize NH_3, and then in anoxic zone, NO_3 is converted to free nitrogen by denitrifying microbes. In SCW, phosphorous is removed by sorption and precipitation. SCW consists of an arrangement of compartments with water regulator which regulate the flow in CW. *Typha species* and *Phragmites australis* are the wetland species commonly vegetated in SCW at the water depth of 20–40 cm. Chen (2011) reported that above 70% removal efficiency for total suspended solids (TSS), chemical oxygen demand (COD) and biochemical oxygen demand (BOD) can be achieved in SCW. The author also reported that removal efficiency of 40–50% for nitrogen (N) and 40–90% phosphorous (P) can be achieved in SCW.

2.3.2 Subsurface Flow CW (SSCW)

Subsurface flow CW (SSCW) is a sort of CW, with saturated or unsaturated vegetation which grow on the gravel. In these CWs, wastewater flows vertically or horizontally by which the pollutants comes into contact with microbes that live around

Table 2.1 Various classifications of constructed wetlands

Wastewater type	Macrophytes	Size	HRT	HLR	Removal, %	References
Surface flow constructed wetland (SCW)						
Synthetic	*Potamogeton crispus* and *Phragmites australis*	100 cm (height) 90 cm (length) 60 cm (width)	5 days	–	COD: 77.7 NH_4^+-N: 92.9 TN: 83.6 TP: 81.4	Zhang et al. (2017)
Synthetic	*P. australis* *Vallisneria natans* *P. crispus*	40 cm (diameter) 50 cm (depth)	10 days	–	COD: 96 NH_4^+-N: 98 TN: 90	Li et al. (2017)
Horizontal subsurface flow constructed wetlands (HSSCW)						
Sewage	*Unplanted*	1.2 m (length) 0.2 m (width) 0.3 m (depth)	5 days	6 cm day^{-1}	COD: 70.3 NH_4^+-N: 18.4 TN: 24.6	Li et al. (2014)
Industrial cork boiling	*Phragmites australis*	0.35 × 0.15 × 0.25 m	5 days	2.6–11.5 g COD/m^2/day	BOD: 91.7 COD: 74.6	Gomes et al. (2018)
Vertical subsurface flow constructed wetlands (VSSCW)						
Synthetic	*P. australis*	60 × 20 cm	72 h	0.207 m^3 m^{-2} $batch^{-1}$	COD: 96 N: 74	Fan et al. (2013)
Domestic	*Canna indica*	60 cm (length) 60 cm (width) 75 cm (depth)	3 days	–	COD: 95 NH_4^+-N: 88 NO_3–N: 50 TN: 83	Ding et al. (2014)

(continued)

Table 2.1 (continued)

Wastewater type	Macrophytes	Size	HRT	HLR	Removal, %	References
Hybrid constructed wetlands (HCW)						
High strength urban	*Phragmites australis*	VSSCW 0.26 m^2 (surface area) HSSCW 125 cm (length) 57 cm (width) 56 cm (depth)	VSSCW: 1.42 h HSSCW: 2.8 days	VSSCW: 344 L/m^2day HSSCW: 64 L/m^2day	VSSCW: BOD: 84 COD: 31 SS: 68 HSSCW: BOD: 62 COD: 66 SS: 84	Herrera-Melián et al. (2015)
Textile industry	*P. australis*, *Dracaena sanderiana*, *Asplenium platyneuron*	VSSCW 1.50 m (diameter) 0.15 m (height) HSSCW 1.01 m (length) 0.45 m (width) 0.7 m (depth)	VSSCW 0.2–1.8 days HSSCW 0.7–7.1 days	566–2830 mm/day and 1132–5660 mm/day	Total efficiency: BOD: 91.7 COD: 74.6 SS: 37.7 NH_4^+-N: 69.9 NO_3–N: 76.6	Saeed and Sun (2013)

HRT hydraulic retention time, *HLR* hydraulic loading rate

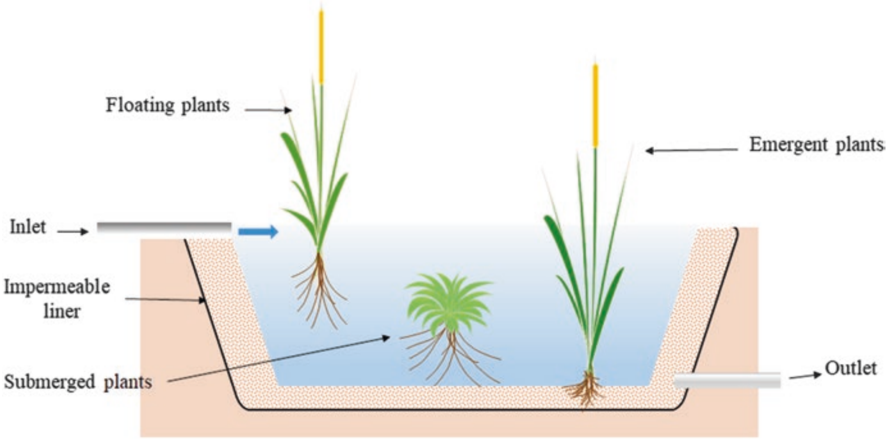

Fig. 2.2 Surface flow constructed wetland (SCW)

the rhizosphere zone (Saeed and Sun 2012). Saeed and Sun (2017) explained about the pollutant removal mechanism of the SSCW as follows: filtration and settling, precipitation and chemical conversion, adsorption on surface of media, plants uptake, organic matter removal by microbes and conversion of nutrients. While removing contaminant, microbial reaction in SSCW is greater than SCW. In SSCW, water flows below the media, and depending on the flow pattern in SSCW, it can be categorized into two groups: (a) vertical subsurface water flow CW (VSSCW) and (b) horizontal flow subsurface water flow CW (HSSCW).

2.3.2.1 Horizontal Subsurface Flow CW (HSSCW)

In horizontal subsurface flow CW (HSSCW), the wastewater enters into the gravel media of CW horizontally and gets treated. Due to subsurface flow, the water is fed into CW below 5 cm from the top layer and not exposed to air. The wastewater reaches into aerobic, anoxic and anaerobic zones. Aerobic zones near the roots drip the oxygen into wastewater (Vymazal 2014). Plant roots release the oxygen which increases the dissolved oxygen (DO) in the upper zone of HSSCW. Lower zone remains as anaerobic region due to poor supply of oxygen. Temperature influences the vegetation activity, while DO content in winter is low but high in summer conditions (Huang et al. 2013). Mburu et al. (2013a, b) reported that horizontal flow decreases the DO level because of high oxygen intake during the degradation. Though nutrient removal is low, HSSCW has been proved very operative in the removal of solids and organics at high rate. Stefanakis (2018) proposed some modifications to advance the efficiency of HSSCW through effluent recirculating, by rising water level or providing step feed and gravity filters. Generally, HSSCW is applied for the treatment of effluents from the industries such as dairy, swine, mine and olive mills. Figure 2.3 represents the horizontal subsurface flow constructed wetland (HSSCW).

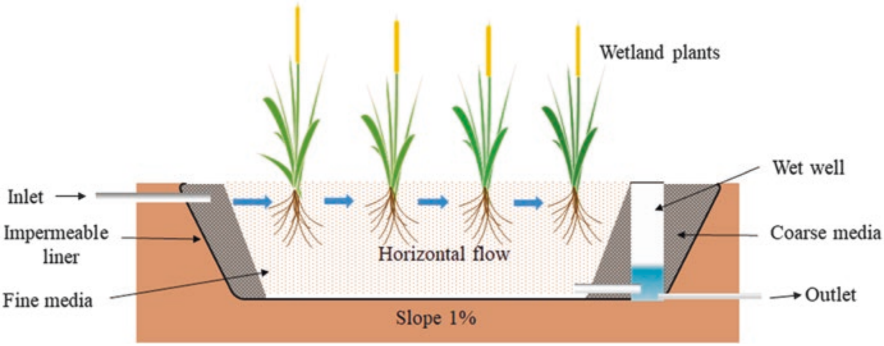

Fig. 2.3 Horizontal subsurface flow constructed wetland (HSSCW)

2.3.2.2 Vertical Subsurface Flow CW (VSSCW)

VSSCW consists of a flatbed topped with gravel and macrophytes planted on the surface of the bed. Wastewater fed into the CW on the top layer and spreads over the other layers of CW. Then wastewater percolates down to reach the outlet through the gravel media due to the gravitational force. In this mode of operation, wastewater moves vertically and shoots out the confined air and pulling the fresh air from the atmosphere into the bed, as a result better aeration is enhanced. In VSSCW, the bed depth varies from 0.45 to 1.20 m and has a slope of 1–2%, which is used to collect the treated water (Stefanakis et al. 2014). For better oxygen transfer in CW, the gravel media is totally drained and permits fresh air to occupy over the media. Oxygen from atmosphere contributes more in bed oxygenation compared to oxygen transferred from the plants. In VSSCW, macrophytes are used to maintain the hydraulic conductivity of the CW. Pempkowiak et al. (2015) reported that VSSCW systems has some advantages such as ability to transport oxygen and significantly smaller than HSSCW systems. Schematic representation of vertical subsurface flow constructed wetland (VSSCW) is shown in Fig. 2.4.

2.3.3 Hybrid Constructed Wetlands (HCW)

For effective wastewater treatment, CWs are combined and form as hybrid CWs. Mostly, HCW consists of the arrangement of VSSCW and HSSCW. Commonly used types of HCW are made up of (a) VSSCW and HSSCW systems in series and (b) HSSCW combined with VSSCW system (Stefanakis et al. 2014). In VSSCW–HSSCW combined system, VSSCW unit placed in first, to remove the suspended solids and organic matter and to provide nitrification. In combination with HSSCW–VSSCW, HSSCW is provided first to remove organic matter and then to achieve denitrification. Then it is followed by VSSCW to enhance the organic removal also to provide good conditions for nitrification. Nguyen et al. (2018) reported that HCW is an efficient treatment method to remove all the pollutants.

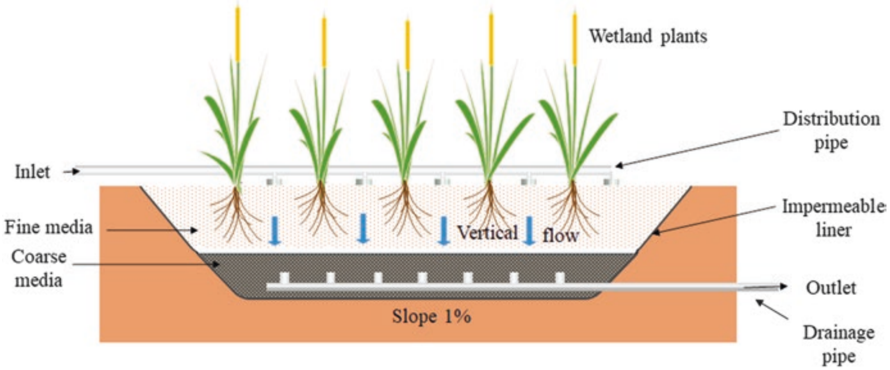

Fig. 2.4 Vertical subsurface flow constructed wetland (VSSCW)

2.3.4 *Advanced CWs*

Other than the main classification of CW, advanced CWs are used to improve organic removal and nutrient removal from various types of wastewater. To achieve efficient removal treatment, improved CWs with artificial aeration, flow with baffle, feed in step mode and flow in circular have been proposed (Wu et al. 2014). Multi-stage CWs comprises more than three stages CWs. For example, Saeed et al. (2012) performed a HCW system that consists of VSSCW, followed by HSSCW and VSSCW. They achieved good removal efficiency of organic materials such as nitrate and phosphorous across the whole hybrid system. Hybrid system of integrated vertical flow CW was introduced to improve the treatment efficiency (Wu 2008). A novel design of HSSCW comprises vertical baffles placed beside the width of CW (Tee et al. 2012). In this design, wastewater is feed into CW as it flows up and down mode and it reaches the outlet. This design type allows wastewater goes in aerobic, anoxic and anaerobic conditions in sequences which allow it to have more contact with rhizosphere. In CW, the recirculation of treated wastewater within the system improves the total nitrogen removal (Stefanakis and Tsihrintzis 2009). This recirculation takes place in well-designed special wetlands, known as circular flow corridor CW (Peng et al. 2012). This wetland avoids the negative influence of particles and colloids on wetland, an advantage of other conventional CWs.

2.4 Factors Influencing the Treatment of Industrial Wastewaters by CW

2.4.1 *Organic Loading*

Effluents from industries such as food processing, dairy industry and distillery contain biodegradable substances and solids. Food processing industry wastes contain oil and grease substances with organic matters as carbohydrates. Due to the presence of high organic content in industrial effluents, CWs are mostly designed for secondary or tertiary treatment after conventional primary treatments through activated sludge (Calheiros et al. 2014). High organic loading in CWs may affect the treatment efficiency and also the wetland vegetation (Wu et al. 2015). Organic loading also influences the growth of vegetations in CW. Plants near the outlet show better growth than inlet of CW. This is because decreased organic loading in wastewater moving towards the outlet might decrease stress on vegetation growth (Worku et al. 2018).

2.4.2 Clogging

Clogging is a factor which influences the CW performance while treating industrial effluents. Clogging mainly depends on the substrate need to be treated and hydraulic characteristics of CW. Knowles et al. (2011) reported that clogging happens because of the gathering of solids on the surface, low porosity, poor hydraulic conductivity, biofilm formation, precipitates of chemicals and vegetation. In CW, microbial substances are detached from each other and develop into biofilm on the surface of the gravel. The biofilm occupies the pores of gravels and slowly develops into block. Due to the continuous growth of biofilm, it forms into layer which clogs the system and fails the wetland system. Indeed, the amount or degree of clogging is influenced by the accumulation of solids, while the clogging is influenced by the hydraulic behaviour of the CW.

High clogging may occur at the inlet of CW, because the wastewater enters through the inlet where the solids filtered and retained. At this zone solids overloaded, form clogs and affects the infiltration rate (Pedescoll et al. 2013). Clogging reduces the oxygen infiltration in the growth media which may reduce the efficiency of CW and significantly shortening the life span of CW (Nivala et al. 2012). Clogging reduces the longevity of CW into 8 years (Nivala et al. 2012) and 13 years (Vymazal 2018), but generally CW has the longevity of more than 20 years. Varga et al. (2013) reported that pretreatment is needed to avoid clogging and for the long-term operation of CW with better performance. Herrera-Melián et al. (2015) reported that pretreatment is needed to reduce the concentration of solids before treating the high strength WW in CW. The author also discussed that COD also in minimum level to reduce the development of biofilm.

2.4.3 pH

In CW, pH influences the microbial processes. As a result of various pollutants in industrial wastewaters, it may either acidic or alkaline. Saeed and Sun (2012) reported that ammonification process in CW takes place when pH is 6.5–8.5. Normally in wastewater heterotrophic production rates are high in neutral pH than in acidic pH. Hadad et al. (2018) reported that free floating species in CW adversely affected if pH goes lower than 3 or beyond 9. The authors also reported that *T. domingensis* is a suitable species in treating industrial effluents with high value pH. The most favourable pH range for treatment of wastewater in CW by macrophytes is 6–9. Worku et al. (2018) also discussed that pH was slightly increased from 6.4 at inlet to 8.1 at outlet while treating brewery industry wastewater. This is due to consuming organic acids by microbes in bioremediation process.

2.4.4 Temperature

Temperature effects the microbial growth and metabolic rates in CW. Normally in CW, greater biological activities and growth rates occur at high temperature while low temperature limits the biological activities and leads to organic accumulation (Meng et al. 2014). The author reported that temperature 28–36 °C is optimum for nitrification activity in CW. Temperature above 15 °C is suitable for ammonia oxidizing bacteria in which the bacteria grows faster than nitrite oxidizing; however, the nitrite oxidizing bacteria can be removed at 25 °C. In CW, 15–38 °C is the most favourable temperature range for the wetland plants.

2.5 Pollutant Removal and Operation and Maintenance for CW Treating Industrial Wastewater

CWs are used to remove the pollutants such as organic and inorganic substances, suspended and dissolved solids, pathogens, metals and nutrients from various industrial wastewaters. CW performance may be affected by wetland structure, hydraulic loading, wastewater type, type of vegetation, pollutant concentration and climatic condition (Trang et al. 2010). In particular, pollutant removal in CW mainly depends upon the organic loading, type of wastewater flow and type of vegetation on CW. More hydraulic retention time is required in CW to remove the pollutants efficiently (Kadlec and Wallace 2008). It is necessary to maintain the level of water for the proper development of vegetation growth. Maintaining an optimum loading for flow of substrate and desired vegetation is needed to get good efficient treatment results in CW, otherwise results may lead to system failure. Plantation in CWs plays predominant role in removing pollutants; the key factors identified are conversion of nutrients, converting to low loaded systems by uptaking nutrients, storing of oxygen in root and releasing of organic carbon (Vymazal 2011b). Table 2.2 shows the performance of pilot scale CW treating various industrial wastewater.

CW plants take a main part in pollutant removal by direct intake, by promoting the particle settling and by providing the substrate to microorganisms that break down pollutants. Adsorption, volatilization, degradation, extraction, filtration and

Table 2.2 Performance of pilot scale CW treating various industrial wastewater

Type of CW	Size of CW	Vegetation	Wastewater treated	Removal, %				References
				COD	BOD	Nitrogen	Phosphorus	
SCW	45.5 m^2	*Phragmites australis*	Olive mill	90	–	87	85	Kapellakis et al. (2012)
SCW	50 × 40 × 0.5 m	*Typha domingensis*	Metallurgical	78.2	82.5	66.1	52.8	Maine et al. (2017)
HSSCW	1.5 × 3.5 × 0.3 m	*Typha angustifolia* and *Canna indica*	Pulp and paper	86.6	80.01	–	–	Rani et al. (2011)
HSSCW	0.6 × 0.5 × 2.0 m	*Lolium multiflorum*	Coffee processing	–	–	69	72	Rossmann et al. (2012)
VSSCW	1.21 × 1.21 × 1.21 m	*Brachiaria mutica*	Textile industry	81	72	84	79	Hussain et al. (2018)
VSSCW	4 m^2	*Arundo donax*	Dairy	–	97.8	53.5	97.1	Sharma et al. (2018)
HCW	VF—0.65 m^2 HF—1.33 m^2	*Phragmites australis*	Tannery	98	98	86	87	Saeed et al. (2012)
HCW	VF—30 m^2 HF—100 m^2	*Canna indica L.* and *Symphytum officinale L.*	Piggery	79	–	63	61	Borin et al. (2013)
HCW	VF—50 m^2 HF—100 m^2	*Phragmites australis* and *Juncus effusus*	Winery	73.3	74.2	55.4	17.4	Serrano et al. (2011)

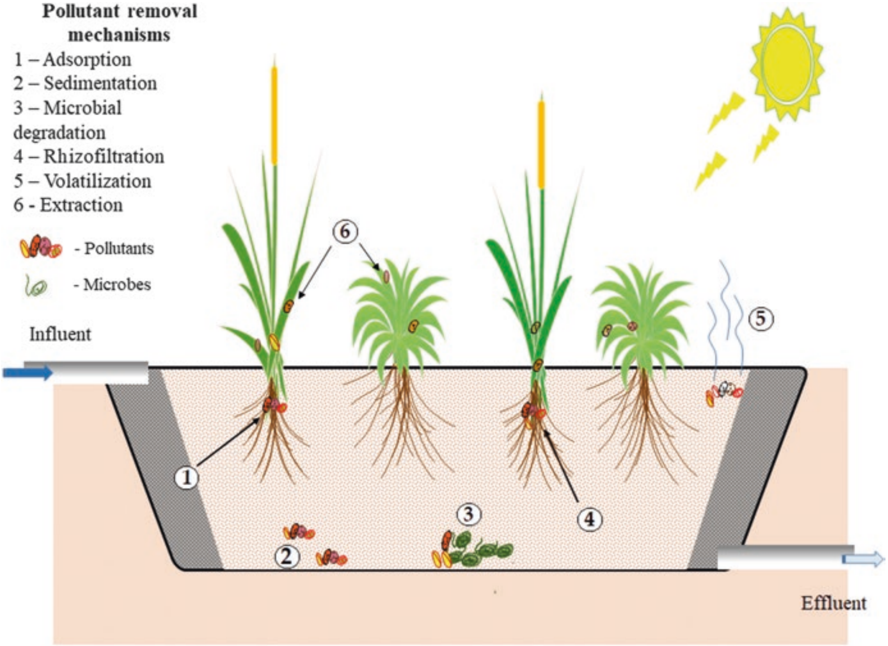

Fig. 2.5 Pollutant removal mechanisms in constructed wetland

sedimentation are the pollutant removal mechanisms take place in CW which is shown in Fig. 2.5. Although nitrogen is removed by various processes like adsorption, volatilization and nitrogen fixation, nitrification and denitrification play a major role in maximum removal of nitrogen in CW compared to other treatment process.

Accumulation of organic matter and development in nutrient removal are promoted due to growth of plants in CWs studied by Tanner (2001) and observed a significant removal of nitrogen treating wastewater (Lv et al. 2013; Chen et al. 2014). HSSF-based CWs treating domestic wastewater was studied by Carballeira et al. (2016) and observed a removal of 91% additional nitrogen, when plotting a graph with the rate of nitrogen removed against the production of biomass. As per plantation and its corresponding reports, it was experimented to be effective in total nitrogen removal, and it ranges from 0.5 to 40.0% (Saeed and Sun 2012). Plants grown above the ground showed sedimentation burial and denitrification which leads to nitrogen removal in CWs with significant improvements (Chen et al. 2014). The increase in nutrient removal shows decline in performance in monitoring the nutrient removal in subsequent year (Zheng et al. 2015). With the help of sedimentation, adsorption, precipitation and dissolution, the microbes in plantation separate phosphorous. Other compounds like phenol are also removed simultaneously.

It was evident that by considering the physicochemical properties, 70% removal was achieved in FCW. Wu et al. (2017) discussed that VSSCW enhances nitrification process by utilizing excess oxygen produced in aeration. Followed by SCW should have a good purpose for ammonia volatilization. Rani et al. (2011) reported about performance of HSSCW treating pulp and paper industry along with the plant species like *Typha angustifolia* and *Canna indica*. The authors also reported that there is a sequential relationship between hydraulic retention time (HRT) and the efficiency of removal. The removal efficiency in low HRT is high as compared to the high HRT. It is possibly due to less supply of nutrients to the microbes at high HRT. Instead, low HRT may lead to the washout of biofilm. Also, the removal efficiency is slightly lower in winter compared to summer. This is because of temperature-dependent microbial activities in CW which are better in summer, because high evapo-transpiration in summer reduces the discharge rate compared with other seasons.

Weerakoon et al. (2013) reported that hydraulic loading rate (HLR) influences the pollutant removal, and it is an important parameter for efficient treatment in HSSCW. The authors constructed a lab-scale HSSCW planted with *T. angustifolia* species which resulted in an efficient removal of pollutants under varying HLR up to 25 cm/day. Appropriate contact of wastewater with the roots of plantation removes the dissolved particles by various microbial communities (Chen et al. 2016). Saeed et al. (2012) performed a HCW system consisting of VSSCW, followed by HSSCW and a VSSCW. The authors used different types of media such as organic coco peat, cupola slag and pea gravel and planted *Phragmites australis* species in HCW. They achieved the removal efficiency of 86% in NH_3–N, 50% in NO_3–N, 98% in biochemical oxygen demand (BOD), 98% in chemical oxygen demand (COD) and 87% in PO_4. Worku et al. (2018) reported the phytoremediation role played by planted species for organic removal in CWs. The authors planted *T. latifolia* and *P. purpureum* in HSSCW for treating brewery industry wastewater, and the removal efficiency of 81% COD and 87% BOD were obtained.

2.6 Economical Consideration of CW for Treating Industrial Wastewater

For the treatment of industrial wastewater through CWs, the investment costs are categorized based on lands, site utility, construction design, earthwork, liners, paving the filtration unit, plantation and equipment dealing with hydraulic monitoring structure, fencing cost and for roads (Wallace and Knight 2006). The proportions of cost for various countries are summarized, and the data available from Vymazal and Kröpfelová (2008) for the United States and the Czech Republic are observed to be in the range of 7–27% followed by Portugal and Spain. The excavation costs ranges between 27 and 53%, liner plantation cost (2–12%), the unit plumbing cost (6–12%), monitoring of structures ranges from (3.1–5.7%) and the mixed costs (1.8–12%).

From economical aspects, the total investment for the CW erection in India was observed to be 29 USD for a square metre (Billore et al. 1999) and evident to be 33 USD per square metre in Costa Rica (Dallas et al. 2004) and proved to be the highest in Belgium with 257 EUR per square metre (Rousseau et al. 2004).

The initial investment cost for subsurface flow CWs is as equal to conventional treatment systems, but the CWs with FWS are comparatively lower due to limited usage of media in rooting of bottom beds. The operation and maintenance costs for CWs are very low compared with concrete and steel technologies. The focus areas monitored were under pretreatment maintenance, less pumping energy, fulfilment in scrutinizing the maintenance work of screens, grit chambers and Imhoff tank and comfort in vegetation harvesting (Kadlec and Wallace 2008). Conservative wastewater treatment plant and activated sludge processes are the effective treatment methods followed in urban areas with economic operation cost. But CWs are affordable for small communities with clear improvement in various aspects such as construction, treatment, maintenance of pumps, vegetation, pest control and less utilization of power. It is observed that only one third of the construction cost occurs in constructing CWs compared to WWTP (Liu et al. 2008).

Comparative study on the economic aspects of CW system and activated sludge process confirm that initial investment cost for CW was relatively half of ASP (Wang et al. 2006). An experimental model CW incorporated with 200 m^{-3} day^{-1} of unit was constructed along Dao River (Beijing, China), and it was estimated that the construction cost was equal to one fifth of that of the existing WWTP (Chen et al. 2008). Land requirement plays a predominant place in deciding the economy of CWs; it is land intensive and normally requires more space (Brissaud 2007); therefore, the expansion in application is progressed to place where land prices are affordable. It is one of the reasonable and cost-effective among all processes, both in case of land availability and in due course with less land requirement. In general it has been constructed only in densely populated areas. In Southern China, an innovative crossbreed CW scheme was constructed with a combination of vertical-baffled flow and HSSF, and this scheme treated domestic wastewater (Vymazal 2011a). The advantage associated with this scheme is that it occupied less land than conventional treatment.

Dallas et al. (2004) constructed a pilot plant treating grey water in Costa Rica, with specialization in cost-effective and energy consumption unit. A comparative study on constructed wetland and a sequential batch reactor (SBR) was performed based on the economic and environmental cost analysis from an industrial wastewater treatment unit by Di Muro et al. (2014). It was observed that the storm water is also routed through the system and the financial result points towards implementing CWs are between the savings meanwhile implementing SBR leads to excessive wastage of multiple of capital amount. The life cycle assessment (LCA) study insists on less energy usage and substance uptake that lead to low eutrophication. Though CWs have some advantages, some limitations need to be considered such as requirement of large area, design criteria for different types of wastewater need to treat and climatic conditions.

2.7 Future Consideration

The water quality standards for wastewater treatments are stricter in coming days, where CWs still need to improve research and development in the area of design and operation. CW implementations are observed to be the reliable treatment technology treating various industrial wastewaters. The sustainability of this treatment system is highly depended on advances in design, which naturally influence the contaminant removal efficiencies and successful operation. In treating high-strength wastewater, the CW performance is observed to be linear and drastic advancement, which is due to framing optimized hydraulic design, method of operation, maintaining proper organic loading and correct selection of substrates and plants. Selection of plants for cultivation in the CWs seems to play a vital role in removing pollutant; hence, proper care must be taken in selecting good species of macrophytes. In general, these species are responsible for eliminating heavy metals and pharmaceuticals through large biomass production, acceptability of high-pollutant loadings with sufficient oxygen and carbon compounds. With toting up non-conventional methods such as wastes from agricultural and industrial by products, with high sorption capacity, needs to be developed and involved in pollutant removal process.

In optimizing the industrial wastewater treatment performance, the parameters such as environment, hydraulic loading and operating conditions play predominant role in forming pathway and mechanism equivalent in pollutant removal. Sustainable technologies such as introduction of diffused aeration, adding external carbon, loading reactor in rhythm, choosing various plant species, amplification of microorganism, choosing variety of substrate, introducing hybrid and baffled flow CWs may be applied for the development and enhancement of CWs treating industrial wastewater. Attention towards selection of suitable plant species which absorbs nutrients and pollutants should be focused because at the time of its death and decay, an appropriate harvest strategies, reclamation and recycling of resources should be disclosed. CWs treating industrial wastewater offer potential for nitrogen removal through anammox and CANON processes.

The process performance and efficiency of this treatment depend on the condition of growth of anammox bacteria and the construction design favouring the replication. In addition the optimized microbial species favouring nitrogen-removing gene should be studied using biogenetics and gene modification. Study on pretreatment methods, planting on new vegetation, introducing different porous media and change in operational strategy are the research areas where future investigation is to focus on for potential innovative applications associated with CWs.

2.8 Summary and Conclusion

For the last five decades, constructed wetland treatment methods have been evolved as a consistent treatment technology treating domestic, industrial and agricultural wastewaters. Special attention has been focused on landfill leachate and storm water runoff. Natural wetlands in general remove pollution, but in CWs the conditions are properly monitored; as a result, the efficiency in pollution removal is drastic. Removing the organics and suspended impurities improves the treatment efficiency also; it is enhanced by adding various types of CWs in combination mode. Introducing special media for the absorption of nitrogen and phosphorous is focused for removal, which are available abundantly and observed to be the major pollutant. The cost for operation and maintenance of CWs are lower as it requires very less power consumption compared with conventional treatment systems. In addition the design is framed in such a way that it is involved in maintaining the environment during floods and provides habitat for wildlife through dual or multipurpose ecosystems.

This chapter illustrates the types of CWs and its operational factors like selection of plant species, specific substrate and level of water to be maintained, rate of loading and hydraulic retention time. They are the key stones to achieve an efficient treatment performance. In the application of CWs, attention should be taken to implement the plant species and specific substrates under real-life condition optimizing the environmental and operational factors in implementing new advanced technologies and maintaining the strategies. The CWs are made to work in all forms of environmental conditions. The organic contents ranging in the form of SS, COD and BOD are proportionally removed based on the application of CWs considering the appropriate design criteria and provided loading rates. CWs are monitored to be the admired alternative technologies rather than conventional type wastewater treatment, and the results treating various industrial effluents almost project the same operational trouble and their margins.

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Chapter 3
Application of Nanoparticles in Environmental Cleanup: Production, Potential Risks and Solutions

Lienda Handojo, Daniel Pramudita, Dave Mangindaan, and Antonius Indarto

Abstract Wastes are unavoidable by-products of human production and consumption activities and have been a primary cause of environmental issues. The release of wastes such as pesticides, textile dyes, and heavy metals that end up polluting environment have endangered not only human health but also biodiversity in general. According to recent developments, the use of nanotechnology for environmental cleanup is evidently promising. Enhanced properties of nanoparticles attributed to their larger surface area enable them to perform in a number of remediation methods such as absorption, adsorption, filtration, chemical reaction, and photocatalysis. This chapter focuses on the applications of four groups of nanomaterials: zero-valent iron nanoparticles, carbon nanotubes, zeolites, and metal oxide nanoparticles for environmental remediation. As a growing research priority, the development of nanotechnology for environmental cleanup has also raised significant concerns on nanoparticle production routes that can be technically challenging. Various fabrication methods ranging from conventional pathways such as physical, chemical, and electrochemical to novel production technique involving biosynthesis are discussed in this review. Despite the useful application, exposures to nanomaterials in the environment also bring potential hazards to plants, animals, and humans. This chapter discusses possible solutions for the aforementioned issue and provides a summary of recent developments of nanoparticle utilization for textile dye and toxic pollutant removals.

Keywords Textile dye · Environmental issues · Nanomaterials · Nanotechnology · Environmental remediation

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3.1 Introduction

Wastes, in a broad definition, can be considered as the main cause of environmental problem. They come from human activities of production and consumption, from home scale to industrial scale. Grey water from these production and consumption activities, as well as black water coming directly from humans, has been the main pollutants of water environment. Common contaminants found in grey water are heavy metals, agrochemicals, oil spills, industrial effluents, toxic gases, and organic compounds. The effects of toxins released from or contained in the wastewater are more severe as their concentration is higher, to the extent that the ecological function of the environment can be seriously damaged. Waste handling and treatment, physically, chemically, or biologically, must thus be carried out in a way that ensures that all toxins could be degraded until the contents are below the maximum allowed. Few examples of concerning contaminants are heavy metals, agrochemicals, oil spills, industrial effluents (Handy et al. 2014), toxic gases (Hyung et al. 2005; Indarto et al. 2008; Indarto 2012), and organic compounds (Indarto et al. 2008).

Pesticides and other agrochemicals, which have been used excessively since the green revolution era, are regarded as one of the main causes of ecosystem problems such as reduced population of insect pollinators (Wells 2007), destroyed bird habitats (Palmer et al. 2007), more threats to endangered species (Miller 2004), and declining biodiversity in general. Chemical pesticides such as chlordane, parathion, malathion, atrazine, and dichlorodiphenyldichloroethylene (DDE) are known for their harmful nature to humans and environment (Rawtani et al. 2018). The fat-soluble nature of these chemicals made them stay longer inside the body of organisms, and this causes an accumulation over the levels in food chain. The problems are made worse because of farmers' tendency to use higher dose than actually required. In humans, the effects of pesticides are seen in neural health problems, cancer, hormonal problems, and even death (US EPA 2014). The agricultural labours are the most vulnerable, with more than a million case of pesticide poisoning found each year (Miller 2004).

One class of the dangerous substances that is usually given special attention is heavy metals. The impacts they potentially cause are great even at low concentration, mostly because they cannot be easily degraded. Cadmium, for example, is a mass produced waste coming from battery, fertilizer, and alloy industries, and it has raised concern over its higher-than-allowed concentration found in drinking water (Mahmoud et al. 2011). Conventional heavy metal removal methods such as precipitation, ultrafiltration, reverse osmosis, and ion exchange are still expensive and are considerably not effective enough when the metal concentration is low (Mahmoud et al. 2011).

Various applications of nanotechnology in energy and environmental sectors are quite promising (Yunus et al. 2012; Christian et al. 2013). Application of nanotechnology for environmental remediation methods such as absorption, adsorption, filtration, chemical reactions, and photocatalysis is promising due to the enhanced properties and performances of nanomaterials. It has the advantages of lower costs and less risk, especially for in situ remediation (Guerra et al. 2018). Common approaches of environmental remediation using nanotechnology are presented in Fig. 3.1. The application can be classified into five big categories: sorbents, filtration, chemical reactions, photocatalysis, and adsorption.

In agricultural sector, applications of nanotechnology, especially the emergence of nano-pesticides and nano-fertilizers, have gained considerable attention. Nanotechnology plays a significant role in the effective management of phytopathogens, nutrient utilization, and controlled release of agrochemicals (Kim et al. 2018). Catalysts are often used in dealing with environmental problem, raising the term environmental catalysis. The application of catalysts can be found in waste treatment, soil and water remediation, emission reduction, and environmentally friendly chemical synthesis. Use of nano-catalysts allows more efficient use of energy and material and leads to less chemical wastes and more effective remediation. In 2009, it was reported that more than 44 sites worldwide had been remediated with the use of nanotechnology (Karn et al. 2009), with two thirds of the sites treated by using nZVI. The number has been rapidly increasing since then. The most common contaminants are Cr(VI), nitrate, and chlorinated compounds such as PCE, TCE, or PCBs.

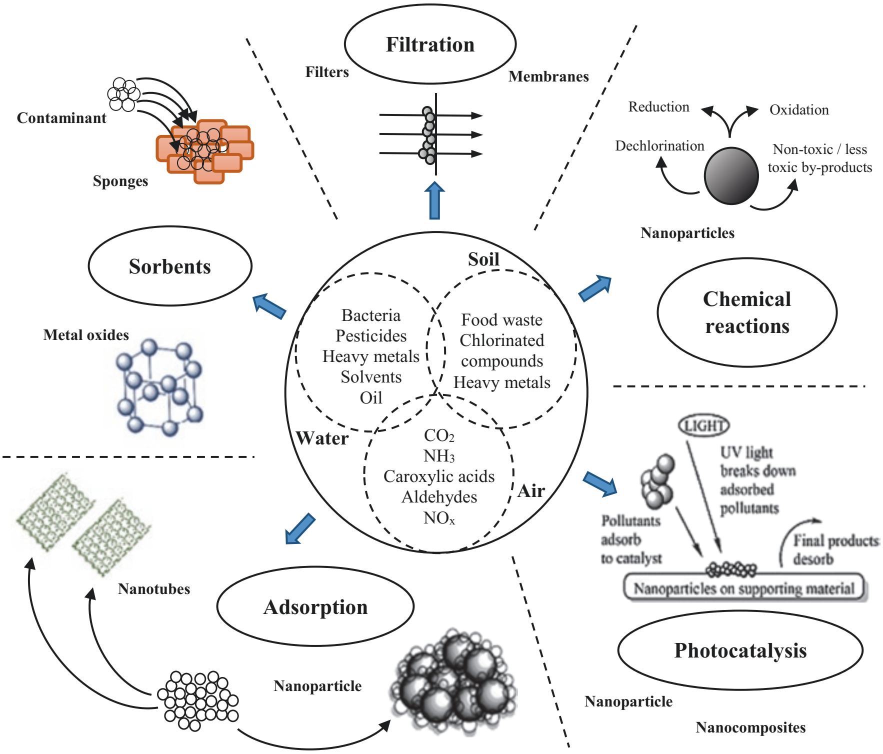

Fig. 3.1 Environmental remediation approaches (Guerra et al. 2018)

Use of nanomaterials for remediation of contaminated soil and groundwater is more quick and cost-effective. Nanomaterials have better adsorption ability due to the high surface-to-volume ratio, as well as better mobility due to the small size. The later characteristic made nanomaterials very suitable for in situ groundwater treatment, because no pumping out of groundwater and no transportation of soil other places are required (Otto et al. 2008).

Researches and utilizations of nanotechnology have been growing rapidly thanks to its potential uses as well as commercialization. The range of applications covers various products, from sophisticated technology product like nano-chips found in computers and other electronic devices to simpler products like paints and lubricants (Ashby et al. 2009).

3.2 A Brief Description of Nanoparticles

The term nanomaterial commonly refers to materials with any external dimension or structure ranging from 1 to 100 nm (ISO TS 8004-1). Further classification of nanomaterial is more loosely defined and has been reviewed in Abdillah et al. (2018). It can be based on physical properties such as the number of dimensions being at the defined nanoscale or the form of the final product. Another classification can be based on the forming material: organic, inorganic, or biological (Kumar and Kumbhat 2016).

Nanomaterials are known for having enhanced or specialized properties that are not found when the materials are engineered at bigger size. Larger surface area and quantum effect have been addressed as the main reasons for this. The large surface area creates a larger number ratio of atoms at the surface to that inside. Interacting directly with the surrounding, the surface atoms have different properties and behaviours compared to the inner ones. The large surface-to-inner atom ratio results in overall properties of the particles that are totally different from that found in macro scale particles. Surface atoms are also less stable than the bulk atoms below them, and as a result, nanomaterials have a more reactive surface (Tantra 2016).

Nanomaterials can be functionalised or engineered to have certain surface functional groups, so that it can target specific substances (pollutants), which make them really efficient for remediation. Its remediating performance can obviously be enhanced by tuning the physical properties. Modifications of the surface groups, structures, sizes, and composition can thus be made to get better or even totally new properties, such as mechanical properties, barrier-permeability, repellent or bonding properties, electromagnetic properties, thermal properties, optical properties, surface reactivity, deliverability, and absorption ability. These peculiar properties are found at certain size range and are non-scalable.

Nanomaterials can manufactured by top-down approach or bottom-up approach. In top-down approach, materials that exist at larger scale are simply made smaller into nanoscale by means of mechanical or chemical processing. Manufacture of the materials at the nanoscale but with the same process used at larger scales also falls into this category. This approach is thus suitable when the bulk properties of the material need to be enhanced but not altered. It is usually used in the production of transistors and in photolithography. The realization of this simple concept is actually technically difficult, costly, and limited by the scale at which material properties do not alter drastically. Bottom-up approach, on the other hand, refers to the process in which the materials are engineered from atomic or molecular level, by means of chemical reaction-based assembly or self-assembly (Kumar and Kumbhat 2016). The materials can be built with even less size limitation and almost without defects. Molecular level assembly also opens the possibility of creating various combinations of biological and inorganic structures, which are not found at larger scales.

3.3 Applications of Nanotechnology for Remediation and the Mechanisms

How nanoparticles enter and are released into the environment is illustrated in Fig. 3.2. The term ‘entry’ refers to the process in which nanoparticles are introduced from outside into the environment, while the term ‘release’ refers to the process of nanoparticle introduction (release) from materials that are already existing in the environment. Nanoparticles can enter the environment from point sources such as production facilities, landfills, and wastewater treatment facilities, as well as from non-point sources, e.g. use of materials containing nanoparticles. Concentration of nanoparticles in the environment can increase when nanoparticle aggregates are formed (Nowack and Bucheli 2007).

Exposure on human can come directly through air, soil, and water or indirectly through animals and plants. One of the health problems associated with nanoparticle entry into human body is decreasing lung efficiency, which leads to asthma and other chronic lung diseases. Polytetrafluoroethylene (PTFE) and carbon-based nanomaterials could potentially cause pneumonia, with stronger response at old ages (Reijnders 2006). There are two variables used to indicate the level of nanomaterial pollution: indicative no-effect concentrations (INECs) and indicative human no-effect levels (INELs). INECs of nanoscale materials, for example, give a threshold limit in the range of ng/L for nano-Ag and nano-ZnO and in the range of μg/L for nano-TiO_2 (Aschberger et al. 2011).

As mentioned earlier, water environment is commonly regarded as the most in need of remediation. There are five mechanisms in water treatment: straining, sedimentation, interception, adhesion, and flocculation (Metcalf and Eddy 2003). In straining, sedimentation, and interception, the media filters pollutants by blocking their flow pathways. The difference compared to adhesion is that the pollutants are simply filtered but not attached onto the media. If the pollutants are small enough, mechanical disturbances can make them flow through the filter. Flocculation, on the other hand, refers to the mechanism in which small pollutants unite into big flocs,

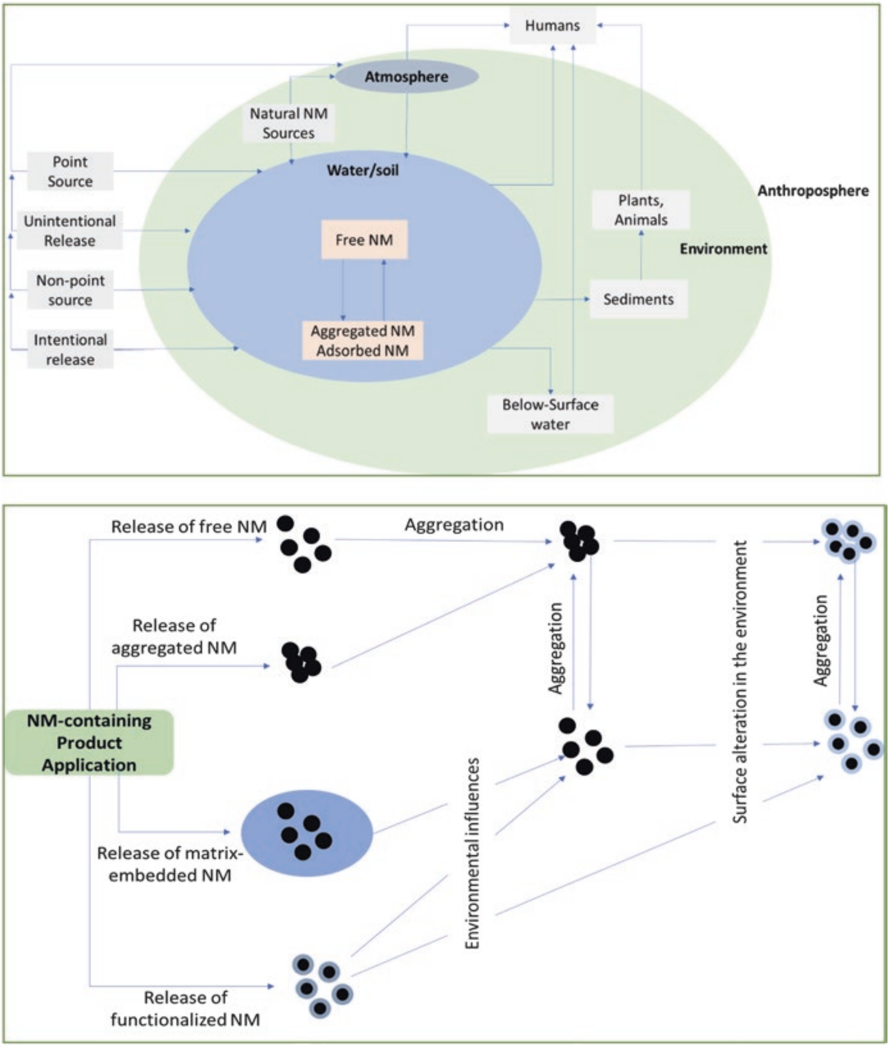

Fig. 3.2 Entry (above) and release (bottom) pathways of nanoparticles into the environment (Nowack and Bucheli 2007)

before attaching to the filter media through another mechanism. Some applications of nanomaterials for water purification are presented in Table 3.1.

Applications of nanoparticles for degradation or removal of textile dyes are tabulated in Table 3.2. The reported data were taken from recent development in the last 2 years (2017–2018) in order to highlight the most advanced nanoparticles for aforementioned particular applications. As shown in the table, the major process for the utilization of nanoparticles for degradation or removal of textile dyes is via photocatalytic process. Generally the degradation of dyes using this method could reach

Table 3.1 Applications of nanomaterials for water purification (reviewed by Annan et al. 2018)

Material	Contaminants	Removal efficiency	References
Adsorption and a combination of adsorption and photocatalysis			
TiO_2	As(III), As(IV) Monomethylarsonic and dimethylarsonic Cd^{2+}	100% 85–95% 142.24 μmol/g	Xu et al. (2007) Gao et al. (2004)
TiO_2/activated carbon	Bisphenol-A	204 mg/g	Lim et al. (2011)
TiO_2/zeolite	Bisphenol-A and intermediate compounds	–	Fukahori et al. (2003)
TiO_2/chitosan	Rhodamine B	94.3%	Zhang et al. (2011)
TiO_2/FeO_3	As(III)	79–80%	Zhou et al. (2008)
	As(IV)	95–99%	
Titanate nanofibers	Sr^{2+}	0.57–0.68 mmol/g	Yang et al. (2008)
	Ba^{2+}	0.95–1.17 mmol/g	
	Pb^{2+}	1.18–1.35 mmol/g	
Fe_3O_4	Cr(IV) As(V)	84.6–99.8%	Hu et al. (2004)
Fe_3O_4/humid acid	Ag(II), Pb(II)	>99%	Liu et al. (2008a, b)
	Cu(II), Cd(II)	>95%	
Fe_2O_3	Cr(IV)	3.86–4.47 mg/g	Zhong et al. (2006)
	As(V)	4.75–5.31 mg/g	
Carbon nanotubes	Atrazine and simazine	>80%	Zhou et al. (2006) Ma et al. (2010) Tofighy and Mohammadi (2011) Kandah and Meunier (2007)
	Anthracene and naphthalene	~100%	
	Cu^{2+}	50.37 mg/g	
	Cd^{2+}	75.84 mg/g	
	Pb^{2+}	101.05 mg/g	
	Zn^{2+}	58 mg/g	
	Co^{2+}	69.63 mg/g	
	Ni^{2+}	12.3–37 mg/g	
Carbon nanotubes—Fe_3O_4 magnetic nanoparticles	Cr(III)	~90%	Gupta et al. (2011); Peng et al. (2005a, b)
	Pb(II)	0.51 mmol/g	
	Cu(II)	0.71 mmol/g	
Carbon nanotubes—ceria nanoparticles	As(V)	78.8–81.9 mg/g	Peng et al. (2005a, b)
Antimicrobial agents			
TiO_2	*E. coli*	7.6% survival ratio	Liu et al. (2008a, b)
TiO_2 shell and nickel ferrite magnetic core	*E. coli*	Decrease in *E. coli* concentration to $<10^6$ CFU/mL	Rawat et al. (2007)
TiO_2/CuO composite	*E. coli* and bacteriophage T4	>9 log reduction	Ditta et al. (2008)

(continued)

Table 3.1 (continued)

Material	Contaminants	Removal efficiency	References
Ag nanoparticles	*B. subtilis*	Susceptibility value of 0.0622 mL/μg	Yoon et al. (2007) Nanda and Saravanan (2009)
		Survival diameter:	
	S. pyogenes	16 mm	
	S. typhi	11 mm	
	K. pneumoniae	0.8 mm	
	V. cholerae	Nil	
	Methicillin-resistant *Staphylococcus epidermidis*	18 mm	
	Methicillin-resistant *Staphylococcus aureus*	17.5 mm	
ZnO	*L. monocytogenes* *Streptococcus mutans*	1.4 log CFU/mL Minimum bacterial concentration of 500 μg/mL	Jin et al. (2009); Hernández-Sierra et al. (2008)
Photocatalysis			
TiO_2	*Acanthamoeba polyphaga* *Candida albicans* *E. coli* *B. subtilis*	>4 log unit reduction 1.7 log unit reduction	Lonnen et al. (2005)
$g\text{-}C_3N_4$	*E. coli*	2×10^7 CFU/mL	Zhao et al. (2014)
TiO_2–ZnO	*E. coli*	2.2×10^{14} CFU/mL bacterial survival	Karunakaran et al. (2011a)
TiO_2–Cd	*E. coli*	Up to 0 CFU/mL survival	Karunakaran et al. (2011b)
Au–ZnO	Methylene blue	Up to 71% degradation	Pawinrat et al. (2009)
Ag_3PO_4	Rhodamine blue	Up to 100% degradation	Ge et al. (2012)
Ag_2CO_3	Rhodamine blue	Up to 100% degradation	Dai et al. (2012)
TiO_2	Reactive yellow 17	94% degradation	Neppolian et al. (2002)
	Reactive red 2	95% degradation	
	Reactive blue 4	88% degradation	
TiO_2	Cr(VI)	79% removal	Chen and Ray (2001) Yoon et al. (2009) Guan et al. (2012)
	Pb(II)	27.2% removal	
	Fe(III)	100% removal	
	Cr(VI)	100% removal	
	As(III)	500 μm As(V) formed from As(III)	
Carbon nanotubed/ZnO nanocomposite	Cyanide	Up to 90% degradation	Saleh et al. (2010)

Table 3.2 Recent development (2017–2018) of nanoparticles for degradation or removal of textile dyes

S. no.	Process	Note 1	Note 2	Nanoparticle type	Core material	Surrounding material(s)	Dyes	% removal	Removal time (min)	Cycles (90%)	References
1	Photocatalytic degradation	Simulated sunlight	300–800 nm, 1500 W Xe lamp	Powder	MnO_2		Rhodamine B	92	40–60		Gagrani et al. (2018)
2	Photocatalytic degradation	Sunlight	NaBH4 (0.01 M)	Composite	NiO	Polyaniline-reduced graphene oxide	Methylene blue	100	11		Ahuja et al. (2018)
3	Photocatalytic degradation	Sunlight		Composite	Au/ZnO/reduced graphene oxide		Methylene blue	>95	30		Juneja et al. (2018)
4	Photocatalytic degradation	Sunlight		Composite	Poly(vinylidene diflouride)-*co*-trifluoroethylene membrane	TiO_2 (P25)	Tartrazine	80	600		Aoudjit et al. (2018)
5	Photocatalytic degradation	Sunlight		Decorated	Graphene nanosheets	Biphasic TiO_2	Methylene blue Congo red	93–98 93–98	60 60		Alamelu et al. (2018)
6	Photocatalytic degradation	Sunlight	11 am–2 pm	Powder	Ni-doped ZnS		Methylene blue	87	180		Jothibas et al. (2018)
7	Photocatalytic degradation	Sunlight		Powder	Titania nanotubes		Rhodamine B Methyl orange	91 87	180 180		Ali et al. (2018)
8	Photocatalytic degradation	UV light	365 nm, 300 W Hg lamp	Decorated	Montmorillonite	Cube-like AgCl	Acid Red 18	>95	3–10	3	Zhang et al. (2018)
9	Photocatalytic degradation	UV light		Powder	Bismuth-doped zinc aluminate		Methylene blue	>90	140		Kirankumar and Sumathi (2017)

(continued)

Table 3.2 (continued)

S. no.	Process	Note 1	Note 2	Nanoparticle type	Core material	Surrounding material(s)	Dyes	% removal	Removal time (min)	Cycles (90%)	References
10	Photocatalytic degradation	Visible and UV light	For RhB: visible, 500 W Xe lamp. For phenol: UV, 500 W Hg lamp	Composite	CdS/carbon quantum dots/ BiOCl		Rhodamine B	100	50		Pan et al. (2018)
11	Photocatalytic degradation	Visible light	>400 nm, 300 W xenon lamp	Bimetallic	ZnS-Ag_2S		Crystal violet Congo red	80 90	50 50		Abbasi et al. (2018)
12	Photocatalytic degradation	Visible light	400–700 nm, 250 W lamp	Composite	WO_3-graphene		Methylene blue	95	70		Ismail et al. (2018)
13	Photocatalytic degradation	Visible light	400–800 nm, 400 W halogen lamp	Composite	Zn/Ti-layered double hydroxide	Ag-layered double hydroxide	Rhodamine B	>90	60		Zhu et al. (2018)
14	Photocatalytic degradation	Visible light	300 W Xe lamp	Core–shell	ZnO ball-in-ball	ZnO ball-in-ball	Methyl orange	100	60		Wang et al. (2017b)
15	Photocatalytic degradation	Visible light	>400 nm, 300 W xenon lamp	Decorated	Flower-like $BiMoO_6$	CeO_2	Rhodamine B Methyl orange	100 100	90 120	6	Li et al. (2018)
16	Photocatalytic degradation	Visible light	300 W halogen lamp	Decorated	Flower-like NiAl-layered double hydroxide microspheres	Black Cu-doped TiO_2 nanoparticles	Methyl orange	>95	60		Jo et al. (2018)
17	Photocatalytic degradation	Visible light	40 W Hg lamp	Decorated	BiOCl	Titania nanotube	Methyl orange	90	480		Buchholcz et al. (2017)

18	Photocatalytic degradation	Visible light	400–800 nm, 150 W tungsten halogen lamp	Powder	Ag-Zr co-doped TiO_2 nanoparticles		Reactive red 194	>95	420		Naraginti et al. (2018)
19	Photocatalytic degradation	Visible light	400 W metal halide lamp	Powder	WO_3 nanorods		Rhodamine B	>90	300	3	Adhikari et al. (2018)
20	Photocatalytic degradation	Visible light	Cool daylight 15 W lamp	Powder	CdS		Congo red Reactive red 141	96 100	80 240		Senasu et al. (2018)
21	Photocatalytic degradation	Visible light, UV, near-infrared	UV: 365 nm, 5 W Visible: 400–800 nm, 300 W Xe lamp NIR: 800–1100 nm, 300 W Xe lamp	Powder	Gd-Sn co-doped $BiFeO_3$ nanoparticles		Congo red Crystal violet Methyl violet	80–90 55–100 23–60	100–200 100–200 100–200		Irfan et al. (2017)
22	Catalytic degradation	$NaBH_4$		Core–shell	Pd or Pt	Ag	Congo red	90	6–7 (Pd@Ag), 13 (Pt@Ag)		Salem et al. (2018)
23	Catalytic degradation	$NaBH_4$		Powder	Montmorillonite	Ag	Methylene blue	>98	7–9	3	Wang et al. (2017a)
24	Catalytic degradation	$NaBH_4$		Powder	Co	With CTAB or PVA	Congo red	>95	6		Bashir et al. (2017)

(continued)

Table 3.2 (continued)

S. no.	Process	Note 1	Note 2	Nanoparticle type	Core material	Surrounding material(s)	Dyes	% removal	Removal time (min)	Cycles (90%)	References
25	Catalytic degradation	$NaBH_4$ 0.001 M		Composite	Reduced graphene oxide	Bimetallic Au-Cu alloy	Congo red Methyl orange Erichrome black T	>95 >95 >95	2 3 5		Rout et al. (2017)
26	Catalytic degradation	$NaBH_4$ 0.01 M		Decorated	TiO_2	Ag, Cu, and Ag-Cu alloy nanoparticles	Rhodamine B Methyl orange	100 100	<1 <1		Saran et al. (2018)
27	Catalytic degradation	$NaBH_4$ 0.2 M		Decorated	Urchin-like TiO_2 nanosphere	Au	Methylene blue, Auramine O, Basic blue 17 Basic red 5	>95 >95	90 30		Ren et al. (2017)
28	Catalytic degradation	Peroxydisulphate		Decorated	N-doped carbon nanofibers	Ni	Orange II	100	40–80	5	Yao et al. (2018)
29	Catalytic degradation	Peroxymonosulphate and $NaBH_4$	For RhB: PMS. For 4-NP: $NaBH_4$	Composite	Carbonized magnetic cobalt-dipicolinic acid coordination polymer		Rhodamine B	>90	30	5	Wu et al. (2018)
30	Adsorption (enzymatic)	Immobilized enzyme (reusable), $q_{max} = 150$ mg/g		Decorated	Fe_3O_4@SiO_2@APS, Fe_3O_4@SiO_2@MPS	Laccase	Methyl red	42–44	900	2	Lin et al. (2017)
31	Adsorption	For BPB, $q_{max} = 41.2$ mg/g. For CV, $q_{max} = 34.5$ mg/g		Core–shell	SiO_2	Poly β-cyclodextrin	Bromophenol blue Crystal violet	50 90	80 80		Chen et al. (2018)

32	Adsorption	$q_{\max} = 180$ mg/g		Composite	Rice-like TiO_2/graphene hydrogel		Methylene blue	>90	40		Liu et al. (2017)
33	Adsorption	$q_{\max} = 302.6$ mg/g		Powder	SiO_2	Dopamine@poly-((3-acrylamido propyl) trimethylam monium chloride)	Congo red	27–52	70–80		Huang et al. (2017)
34	Ultrafiltration	Transmembrane pressure 5 bar, flux 100 L/mh^2		Composite	Clay-alumina ceramic membrane	Titania nanoparticles (lumen side)	Alizarin red	100	100		Oun et al. (2017)
35	Organic solvent nanofiltration	Permeance 0.39 L/m^{2}h bar (RB), 3.07–3.62 L/m^{2}h bar (SB35)		Composite	P84 polyimide/dopamine/POSS	POSS	Rose Bengal	99			Xu et al. (2017)

high removal performance from 90 to 100%, under reasonable duration (mostly below 300 min). The interesting properties of the photocatalytic degradation of textile dyes in 2017–2018 are the dominance on the quest of honing the potential of visible light, especially sunlight. The developed nanomaterials or composites could destruct several problematic dyes such as rhodamine B and crystal violet and also the popular model dyes such as methylene blue, Congo red, and methyl orange.

Besides the photocatalytic process, there is also catalytic degradation process, which is mainly accompanied with $NaBH_4$ as a strong reducing agent that assists nanoparticles to destruct the dyes. Less popular oxidizing agents that also synergistically break down the harmful dyes via catalytic degradation process are peroxydisulphate and peroxomonosulphate. Different approaches could also be taken to treat the textile dyes in water. The conventional adsorption processes treat the wastewater having textile dyes by adsorbing them into the particles, with uptake capacity ranging from 30 to 300 mg dyes/g nanoparticles. An emerging technology of membrane separation follows a different strategy that is rejecting the dyes in the aquatic phase in order to obtain clean water, with promising rejection of nearly 100%.

From the perspective of the nanomaterials, there are several forms of nanoparticles for the degradation or removal of textile dyes, i.e.

(a) Powder (single core, with or without doping)
(b) Bimetallic (a core composed of two metals)
(c) Decorated (core nanoparticles covered with smaller particles)
(d) Core–shell (core nanoparticles completely covered with other particles)
(e) Composite (core nanoparticles were embedded onto a surface larger than the nanoparticles)

The single cores (powder nanoparticles) in Table 3.2 mostly consist of period 4, 5, and 6 transition metals, e.g. Co, Ni, Pd, Pt, and W, beside the commonly used Ti, Au, Ag, and Cu. While the single-core type is quite common due to the simple fabrication, the recent developments in the last 2 years also open new avenues for the composite type and the decorated type. They enable the use of polymeric and carbonic materials to join force to perform environmental remediation. The employment of these nanoparticles was partially assessed from the point of view of how many cycles that the nanoparticles could withstand and maintain 90% of the degradation or removal performance, which are quite limited in number of reports, ranging from 2 to 6 cycles only. This constraint could be a motivation for improvement in the near future.

Applications of nanoparticles for removing or degrading aromatic pollutants, such as chlorophenol, nitrophenol, bisphenol A, polyaromatic hydrocarbons, and also several antibiotics are tabulated in Table 3.3. Similar to the previous discussion, the main process for degradation utilizing nanoparticles is photocatalytic degradation using visible light, followed by catalytic degradation together with $NaBH_4$, peroxomonosulphate, or peroxidisulphate. The performance of the nanoparticles in degrading the aromatic pollutants are 80–100%, as fast as <10 min, up to 150 min (although for some cases may reach >1000 min). Preferred metal for this application is Ti and also group 1B of transition metals (Ag, Au, and Cu).

Table 3.3 Recent development (2017–2018) for nanoparticles for degradation or removal of organic pollutants

No.	Process	Note 1	Note 2	Nanoparticle type	Core material	Surrounding material(s)	Other pollutants	% removal	Removal time (min)	Cycles (90%)	References
1	Photocatalytic degradation	Simulated sunlight	35 W Xe lamp	Composite	Ag-AgBr/reduced TiO_2 nanotube arrays		4-chlorophenol	100	120		Cheng et al. (2018)
2	Photocatalytic degradation	Sunlight		Composite	ZnSe-WO_3/gum		Bisphenol A	>95	90	6	Kumar et al. (2017)
3	Photocatalytic degradation	Visible and UV light	For RhB: visible, 500 W Xe lamp. For phenol: UV, 500 W Hg lamp	Sandwich	CdS/carbon quantum dots/ BiOCl		Phenol	100	120		Pan et al. (2018)
4	Photocatalytic degradation	Visible light	>400 nm, 300 W xenon lamp	Bimetallic	ZnS-Ag_2S		Polyaromatic hydrocarbons (naphthalene, phenanthrene, pyrene)	80–90	90		Abbasi et al. (2018)
5	Photocatalytic degradation	Visible light	>400 nm, 300 W xenon lamp	Decorated	Flower-like $BiMoO_6$	CeO_2	Tetracycline	80	120	6	Li et al. (2018)
6	Photocatalytic degradation	Visible light	300 W halogen lamp	Decorated	Flower-like NiAl-layered double hydroxide microspheres	Black Cu-doped TiO_2 nanoparticles	Isoniazid	90	120	5	Jo et al. (2018)
7	Photocatalytic degradation	Visible light	400–800 nm, 150 W tungsten halogen lamp	Powder	Ag-Zr co-doped TiO_2 nanoparticles		Sulphamethox azole	>90	420		Naraginti et al. (2018)

(continued)

Table 3.3 (continued)

No.	Process	Note 1	Note 2	Nanoparticle type	Core material	Surrounding material(s)	Other pollutants	% removal	Removal time (min)	Cycles (90%)	References
8	Photocatalytic degradation	Direct sunlight	2 × 12 h (6 am–6 pm)	Core-shell (ethanolic (70%) extract of *Azadirachta indica* leaves)	ZnHCF (zinc hexacyanoferrate) nanocubes	Fe_2O_3	Chrysene	80	1440		Rachna et al. (2018)
9	Catalytic degradation	$NaBH_4$ 0.01 M		Decorated	TiO_2	Ag, Cu, and Ag-Cu alloy nanoparticles	4-Nitrophenol	100	<1		Saran et al. (2018)
10	Catalytic degradation	$NaBH_4$ 0.001 M		Composite	Reduced graphene oxide	Bimetallic Au-Cu alloy	4-nitrophenol	>95	1–7		Rout et al. (2017)
11	Catalytic degradation	Peroxomono sulphate		Core–shell	Dopamine-coated CoFe	Cr Mn Fe Co Ni Cu Zn	*o*-, *m*-, *p*-Nitrophenols				Goyal et al. (2018)
12	Catalytic degradation	Peroxymono sulphate, and $NaBH_4$	For RhB: PMS. For 4-NP: $NaBH_4$	Composite	Carbonized magnetic cobalt-dipicolinic acid coordination polymer		4-Nitrophenol	>90	30	5	Wu et al. (2018)
13	Adsorption	q_{max} 84.55 mg/g		Decorated	Clay	MgO	Metronidazole	97–100	150		Kalhori et al. (2017)

3.4 Common Groups of Nanomaterials Used for Remediation

Nanoparticles utilized for environmental cleanup can be classified based on their base materials. Four big groups are considered here: metal oxide nanoparticles, carbon nanotubes, zeolites nanomaterials, and nanoscale zero-valent iron (nZVI).

3.4.1 Nano Zero-Valent Irons

Nano zero-valent irons (nZVI or Fe^0) are iron-based nanoparticles with a core of Fe^0 and an outer shell of Fe oxides. Reduction effects are made possible by two electrons that are released when Fe^0 reacts with oxidizing agent and alter its oxidation state into ferrous ions (Fe^{2+}). The process is repetitive and takes place during the remediation. Major chemical reaction pathways of nZVI are illustrated in Fig. 3.3. They are corrosion of ZVI, precipitation of Fe(II) and Fe(III) oxyhydroxides, and transformation of Fe oxides in solid phase (Shi et al. 2015).

nZVI reacts very effectively with contaminants and are very stable and difficult to decompose with energetic or thermal treatment (Indarto et al. 2006a, b). Moreover, nZVI can reduce both organic and inorganic contaminants, making it effective as reducing agents in micro and macro scales. Another advantage is its high mobility, which allows easier and more direct injection into below ground, underneath buildings, contaminated plumes, and shallow and deep aquifers. A study has shown how effective the material is in dealing with the pollutants thanks to its faster movement and ability to move with groundwater, which makes treatment over larger areas possible (Mace et al. 2006). The costs of nZWI and other iron-derived nanomaterials are not expensive, in the range of $50–100 per kg.

The use of the more mobile nano-sized ZVI over its macro-sized counterpart has been shown to eliminate the need for a permeable reactive barrier (PRB), which is

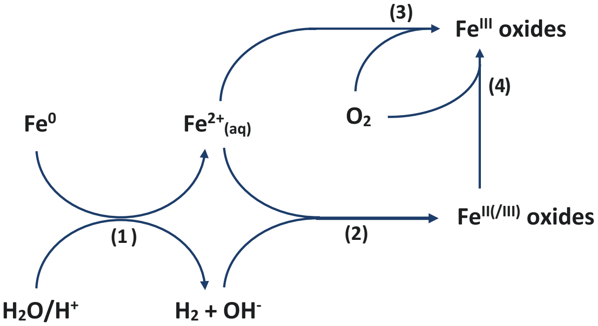

Fig. 3.3 The major chemical reaction pathways of nZVI: (1) corrosion, precipitation of (2) Fe(II) and (3) Fe(III) oxyhydroxides, and (4) transformation of Fe oxides (Shi et al. 2015)

previously a very popular utilization of ZVI for remediation of groundwater and contaminated sides. This old technology has a downside that it can only deal with contaminant that flow through the barrier and does not directly address the contaminating sources (ITRC 2011). The effectiveness is also reduced by sedimentation that occurs often due to its macro-size. Since then the nZVI has become the most commonly used nanomaterial for soil and groundwater remediation (Karn et al. 2009). According to a study by PARS Environmental Inc. (2004), remediation of a single site using pump-and-treat method would cost \$4,160,000 for nZVI and \$2,200,000 for PRB.

Some of the contaminants that can be reduced with nZVI include excessive dissolved oxygen, dyes, brominated methanes, and trihalomethanes. It has been reported effective in removing chlorinated substances such as methanes, ethanes, hydrocarbons, benzenes, and other polychlorinated hydrocarbon pesticides (Zhang 2003), as well as dissolved metals such as Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cr^{6+} (Sun et al. 2006). Others reported their utilization in reducing nitrate (Liou et al. 2006; Sohn et al. 2006), arsenate and arsenite (Jegadeesan et al. 2005; Kanel et al. 2005, 2006), perchlorate, chlorate, and chlorite (Cao et al. 2005), and chromate (Manning et al. 2007). nZVI can be produced from various methods. Physical methods such as grinding, abrasion, and lithography are among the first generation, followed by phase separation, high temperature annealing, and nucleation from homogeneous solutions or gas (Shan et al. 2009).

More recent and frequently used route for nZVI production is chemical reactions. This method has the advantages of being way simpler and capable of producing a homogenous and highly reactive structure (Jamei et al. 2013). An example is by using sodium borohydride ($NaBH_4$) as a reducing agent, according to the following reaction (Wang and Zhang 1997):

$$Fe\left(\mathrm{H_2O}\right)_6^{3+} + 3\mathrm{BH_4^-} + 3\mathrm{H_2O} \rightarrow Fe^0 \downarrow + 3\mathrm{B}\left(OH\right)_3 + 10.5\mathrm{H_2}$$

Other routes are reduction of goethite (a-FeOOH) or hematite (a-Fe_2O_3) with hydrogen at high temperature (Nurmi et al. 2005) and decomposition of iron pentacarbonyl ($Fe(CO)_5$) in organic solvents or argon (Sun et al. 2007).

Alternative methods of nZVI synthesis that are not yet popular but possess some unique advantages are precision milling, carbothermal reduction, enhancement by ultrasound assistance, electrolysis, and biosynthesis (Stefaniuk et al. 2016). Precision milling has the advantages of no needs of any toxic reagents like needed in chemical synthesis, and the applicability on a large scale (Li et al. 2009). Carbothermal reduction of iron compounds requires cheap and easily available materials and is simple. In this method, nanoparticles of iron oxides or hydrous Fe^{2+} salts are reduced to nZVI with the help of gaseous reducing agent and high temperature of above 500 °C (Crane and Scott 2012).

Application of ultrasound made it possible to get a smaller particle size (Tao et al. 1999) and different morphology from spherical, plate, to needle by changing the frequency (Jamei et al. 2014). Electrolysis is very simple, faster, and cheaper compared to chemical reduction methods, although there is tendency of the produced iron atoms to aggregate and form a cluster. Ultrasonic waves and cationic surfactants as a stabilizing agent can be used to overcome this problem (Li et al. 2009). Lastly, biosynthesis route, which is utilization of plant extracts to reduce metal compounds into nanoparticles, is promising because it needs no high pressure or temperature, is environmentally friendly, inexpensive, easy to implement on large scale (Machado et al. 2013, 2014).

3.4.2 Carbon Nanotubes

Carbon nanotubes (CNTs) are carbon-based nanomaterials made of a surface tube and hexagonal arrays of carbon atoms, with specific absorption sites (Agnihotri et al. 2006). Being one of the most researched and produced nanomaterials, CNTs have been effectively used as nanosorbents for soil and groundwater pollutants. Removal of heavy metals like Cr^{3+}, Pb^{2+}, and Zn^{2+}, metalloids like arsenic compounds, volatile organic compounds, and other organic and inorganic pollutants from soil and groundwater with CNTs has been reported (Li et al. 2016). This is attributed to its highly porous and hollow structure, large specific surface area, light mass density, and strong interaction. The main drawback of CNTs is that they are still more expensive than other nanomaterials that are used for remediation.

There are types of CNTs according to their structure: single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), carbon beads, carbon fibres, and nanoporous carbon (Gadhave and Waghmare 2014). Use of SWCNTs and MWCNTs as sorbent is very common in the removal of heavy metal from groundwater. Compared to granular activated carbon, another popular sorbent, the SWCNTs and MWCNTs have better capability in absorbing Ni^{2+} in groundwater (Lu et al. 2008).

3.4.3 Zeolites

Zeolites are actually a quite common material used for various purposes. Nanomaterials from zeolites benefit from the high availability and low price, making them stand out among other nanomaterials (Eyde 2010). Zeolites are characterized by the unique structural features of channels and pores, which not only make them lighter than other materials (Liu and Lal 2012a), but also allow introduction of new functional groups, which improves substantially its activity and selectivity for the removal of several substances (Inglezakis and Grigoropoulou 2004). The modification can be made on natural zeolites. Removal of pollutants with zeolites is usually done by adsorption processes, through anion uptakes from the effluents (Haggerty and Bowman 1994). Performance-wise, the most outstanding is their ability of hydration-dehydration and cation exchange with aqueous solutions without really changing the structure, and the high cation-exchange capacities, up to 300 $cmol_c\ kg^{-1}$ (Ming and Allen 2001). This ion exchange capacity also makes zeolites a good fertilizer. A study by Xiong et al. (2015) showed that the remediating effect of nano-sized zeolites was better than that of macro-sized zeolites.

Use of natural and synthetic zeolites as potential remediation agent for heavy metals in soil has been reviewed by Ming and Allen (2001). Uptakes of the heavy metals are reduced by immobilization. For monovalent heavy metal cations of low charge density and divalent cations with lower hydration energy, most natural zeolites can be used as the remediation agent (Colella 1996). Ca-type zeolites are preferred to Na-type zeolites as remediating agent if the contaminated soil is intended for revegetation (Liu and Lal 2012a). Equipped with high selectivity to heavy metals and good ion-exchange capacity, zeolites have the potential for dealing with heavy metals found in ex-mine soil as well.

Moreover, zeolites are also known for the ability to improve physical structures and properties of soil, which is attributed to their unique structural features and size (Liu and Lal 2012a). While adsorbing toxins, zeolites improve the soil structure with increased clay-silt fractions. The overall soil density is reduced with the low density of zeolites. As a result, the soil is more arable, and its water holding capacity is increased, which in turn increases the availability of water and nutrients, or in other words, the soil fertility (Ming and Allen 2001). Poor structures, high bulk density, and low water holding capacity are the common problems found in ex-mine soil. Remediation with zeolites can thus recover the fertility of ex-mine soil and make it possible and safer for plantation and other utilizations. The ability of zeolites to increase the soil's overall pH and nutrient-holding capacity, although still inferior than that of liming materials, is due to the extraordinary capacity in exchanging the H^+ ions with the Ca^{2+} ion (Liu and Lal 2012b; Ming and Allen 2001). Another experimental study by Xiong et al. (2015) shows how application of zeolites could increase soil pH and decrease the concentration of exchangeable Cd in soil and plant.

Zeolites are highly cost-effective in treating solid and liquid wastes in industry and municipality (Liu and Lal 2012a). Depending on the activated compounds present in it, nano-zeolite has the average price of around \$145–\$8000 per tonne. In a study by Zorpas et al. (2000), the ability of zeolites in absorbing toxic metals (Cd, Cu, Cr, Ni, Pb, and Zn) in solid wastes has been proved. Pasini (1991) reported the use of zeolite for the removal of NH^{4+} from municipal and industrial wastewater. Reduction of eutrophic potential of water by phosphate ions and ammonium removal using zeolites has also been carried out in some projects (Ming and Allen 2001). Zeolites can also remove trihalomethanes formed during the disinfection process by chlorine (Ulucan et al. 2013).

3.4.4 Metal Oxides

Metal oxide nanoparticles are known for its effectiveness in bonding with metal ions in contaminants (Liu and Lal 2012a), making them popular as adsorbents for remediation. Common examples are hematite (α-Fe_2O_3), magnetite (Fe_3O_4), and goethite (α-FeOOH), which are naturally present in soil. They act as iron catalyst in hydrogen peroxide oxidation of organic compounds in a soil remediation process (Kong et al. 1998).

The characteristics that make iron oxides effective remediating agents are strong adsorption, large retardation factor, and resistant desorption, which are mainly due to their large surface area (Shipley et al. 2011). It is important to modify their surface to improve their activity and avoid aggregation that may decrease the adsorption efficiency. The modification can be performed by attaching suitable functional groups such as silanol, thio, amine, carboxylic and phosphoric acid, polymer, biomolecules, small organic molecules, and other metal nanoparticles (Dave and Chopda 2014). Coexistence with other assisting materials is another way to improve their performance. For example, the presence of Zn(II) has been shown to enhance the adsorption ability of iron oxides at base soil condition (Carabante et al. 2012).

3.5 Risks of Nanotechnology Application: Cases and Management

Use of nanoparticles for remediation actually possesses a great risk, which is mostly dose-related. Wang et al. (2011), for example, observed the impact of accumulating nano-Al_2O_3 in *Ceriodaphnia dubia*, a species of water flea commonly found in freshwater. Interaction of nano-Al_2O_3 with As (V) is known to increase its toxicity drastically. The materials used for the remediation could potentially become pollutants themselves when they are released to the environment.

High mobility of nanoparticles can be considered a double-edged sword. As easily as they can reach hidden areas, nanoparticles can be over-exposed easily and bring serious damage to the surrounding areas that are actually healthy. Iron oxide nanomaterials, for example, have low solubility and may easily spread bound toxic materials such as copper, which is just second to mercury in toxicity level to algae, phytoplankton, and some plants (Sposito 1989). A study by Auffan et al. (2006) shows how long-term effects such as mutation are triggered in organisms with high exposure to the nanoparticles. Other harmful potentials such as their radical properties need further study.

Side effects of nano-zeolites as remediating agent have not been much studied. While large-sized zeolites are considered non-toxic and thus environmentally friendly, it is still unclear whether at nano-size they possess harmful effects to the environment (Lehman and Larsen 2014). Kihara et al. (2011) showed that nano-sized zeolites have a considerable level of toxicity. Such is not the case with purely siliceous zeolites. Differences in morphology, rather than the surface charge, are said to be the reason. Another example in which useful properties of zeolite can bring such negative effects can be found in applications with vegetation. Cation exchange in plant rhizosphere, which supposedly enhances nutrition absorption, might also result in toxicity due to overexposure to metal ions that come from the zeolites. This can be prevented by preconditioning zeolites into their safer forms, for example preconditioning Na-zeolites to their ammonium form to prevent sodium toxicity. The opposite cases like too much binding of nutritionally important metal ions may bring degradation instead of improvement. Use of zeolites must thus be well designed according to the specific selectivity to the metals to be immobilized.

Just like the case with other nanomaterials, nZVI application also possesses some technical challenges caused by their characteristics. Its use for in situ remediation is limited by microscale aggregation caused by the weak surface charges of Fe nanoparticles. The aggregation is known to reduce the mobility, durability, and mechanical strength of nZVI influences. There have been some efforts to improve material properties by modification (Quinn et al. 2005; Mueller et al. 2012; Fei et al. 2012; Kim et al. 2013; Quan et al. 2014), such as use of metal catalysts such as Ni, Cu, Pd, Pt, Ag, and Au to produce bimetallic nZVI, amorphous type of nZVI, and coating with food-grade surfactant to create emulsified nZVI. Other examples are carbon-supported nZVI, sepiolite, zeolite, and attapulgite. Broad and massive application of nZVI for remediation could in turn create another pollution problem. nZVI redox reaction generates nanoscale Fe oxides that are low soluble. If adsorbed by cells, the oxides can interfere with biological systems and cause cell mutation or even death (Auffan et al. 2006).

Setting up a guideline for nanotechnology application for healthy environmental remediation process is therefore a big task to be done. Some organizations and institutes have been established to deal with the issues related to safe uses and environmental impacts of nanotechnology. Nanotechnology Core Facility (https://www.fda.gov), for example, is an institute established by collaboration of National Center for Toxicological Research (NCTR), which is a research centre under the US Food and Drug Administration (FDA), and the Office of Regulatory Affairs (ORA). Its mission is to ‘support nanotechnology toxicity studies, develop analytical tools to quantify nanomaterials in complex matrices, and develop procedures for characterizing nanomaterials in FDA-regulated products’. Similar step has been made by the US Department of Health and Human Services by setting up the so-called National Toxicology Program (NTP) Nanotechnology Safety Initiative (NTP 2006). The program is aimed at potential human health hazards associated with the manufacture and use of nanoscale materials. The US National Institute for Occupational Safety and Health (NIOSH) published a report in 2009 titled ‘Approaches to Safe Nanotechnology: Managing the Health and Safety Concerns Associated with Engineered Nanomaterials’ (NIOSH 2009). The report provides comprehensive information related to the health and safety issues when working with or being exposed to nanomaterials.

In Europe, the European Commission considered nanotechnology one of key enabling technologies (KETs). Joint Research Center of the European Commission has been actively carrying out researches related to nanotechnology applications and its impacts on human health and environment. It focuses on the development of methods for assessing and characterizing nanomaterials, and methods for analysing their interactions with biological systems. The research group acts as the main advisor in the making EU's nanotechnology-related policies, by contributing to the development of tools, databases, and regulations. A comprehensive review on the regulatory aspects and research needs in Europe Union has been published by Rauscher et al. (2017).

To answer the problem of nanomaterials potentially becoming pollutants themselves, development of biodegradable nanomaterials have been encouraged (Guerra et al. 2018). The approach of this green fabrication may vary from utilizing extract of plants or fruits, immobilizing enzymes in order to improve the recyclability, and employing microorganisms. Liu and Lal (2012a) recommend mixing the nanoparticles with small quantities of conventional amendment materials such as fly ash, manures, composts, or biosolids. This practice is similar to that found in fertilizer application in agricultural soil. Before application for soil remediation, the mixture must be stabilized to a certain degree, and the heavy metals and toxin contained in it must be completely removed.

A new class of green-fabricated nanoparticles for dye removal is tabulated in Table 3.4. The produced nanoparticles were also in par with those prepared via conventional routes, with the removal of several dyes from 60 to 95%, in 1.5–600 min through photocatalytic and catalytic degradation processes. Moreover, some nanoparticles are in the inception phase of novel degradation process (enzymatic degradation and biogenic process) which may consume more than 1000 min to perform well (80–95% degradation).

3.6 Conclusions

It has been shown how promising the application of nanotechnology for environmental cleanup is. Enhanced properties attributed to their larger surface-area-to-volume ratio allow them to perform better than the more common larger particles in many remediation processes. The potential and spectrum of the applications have brought them to a level that makes nanomaterials for cleanup a top priority for research. The risks associated with the utilization of nanomaterials have raised some concern. However, they are answered with the advancement in novel production and application methods, as well as movements to ensure safer utilization. Despite all the risks and drawbacks, remediation using nanomaterial still has bright future especially for large contaminated sites because it can significantly reduce cleanup time, has very high contaminant reduction rate and effectivity, more efficient, and more practical.

Table 3.4 Recent development (2017–2018) of green-fabricated nanoparticles for degradation or removal of textile dyes

No.	Process	Note 1	Note 2	Nanoparticle type	Core material	Biological component	Dye	% removal	Removal time (min)	References
1	Photocatalytic degradation	Sunlight		Powder	Fe_2O_3	Ficus carica extract	Acid blue	87	360	Tharunya et al. (2017)
2	Photocatalytic degradation	Visible and UV light	For MO: 450 nm, 8 × 40 W. For CBBG-250: UV, 365 nm, 2 × 40 W	Powder	Ag	Ethanolic (70%) extract of Psidium guajava L. leaves	Methyl orange Coomassie brilliant blue G-250	60 70	600 360	Wang et al. (2018a)
3	Catalytic degradation	Peroxodisulphate and peroxomono sulphate		Powder	Cu	Extract of Azadirachta indica leaves	Methyl orange	>80	30	Nagar and Devra (2017)
4	Catalytic degradation	$NaBH_4$ 0.1 M		Powder	Pd	Carboxymethyl cellulose	Scarlet 3G Reactive yellow 179	93 91	1.5 4.5	Li et al. (2017)
5	Catalytic degradation	Bio-Au NP as catalyst, 303 K, shaking 150 rpm		Powder	Au	Trichoderma sp. WL-Go	Acid brilliant scarlet GR, acid red B, acid orange G, acid black 1, reactive red X-3B, reactive black, reactive red, cation red	41–94	100–180	Zazouli et al. (2017)
6	Biogenic reaction	Pd + *K. oxytoca*		Powder	Biogenic Pd nanoparticles	Biogenic reaction involving *Klebsiella oxytoca* GS-4-08 (CGMCC 5237)	Acid blue 113 Reactive black 5 Methyl orange Acid red 1	>95 >95 >95 >95	1440–2880 1440–2880 1440–2880 1440–2880	Wang et al. (2018b)
7	Enyzmatic reaction	40 °C		Decorated	Fe_3O_4	Laccase, TEMPO	Acid fuchsin	Up to 80%	1080	Gao et al. (2018)

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Chapter 4
Efficiency of Algae for Heavy Metal Removal, Bioenergy Production, and Carbon Sequestration

Ankit, Nirmali Bordoloi, Jaya Tiwari, Sanjeev Kumar, John Korstad, and Kuldeep Bauddh

Abstract Environmental contamination is one of the paramount concerns engulfing the entire world. Being nondegradable in nature, heavy metals (e.g., Ni, Cd, Cu, As, Hg, and Pb) are significant pollutants of soil and aquatic ecosystems. Although numerous technologies have been employed to remove toxic metals from contaminated sites, there is still need for more efficient and ecologically sound methods. The use of algal species for the removal of heavy metals as well as other contaminants like dyes, nutrients, ions etc. from water and wastewater, which is popularly known as phycoremediation, has been found to be eco-friendly, ecologically sound, and a value-added tool. The common algal species which are being used for phycoremediation are *Chlorella*, *Scenedesmus*, *Oscillatoria*, *Lyngbya*, *Gloeocapsa, Spirulina*, *Chroococcus*, *Synechocystis*, and *Anabaena*. The use of algae for the removal of pollutants also helps in carbon sequestration and biofuel production. This chapter discusses the removal of toxic metals from contaminated aquatic ecosystems using various species of micro- and macroalgae along with factors that influence the process of phycoremediation and the role of algae in biofuel production and carbon sequestration.

Keywords Biofuels · Heavy metals · Microalgae · Macroalgae · Wastewater · Phycoremediation

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4.1 Introduction

Industrialization and urbanization have caused overload of contaminants into the environment. In the last few decades, the pollutants have led to deterioration of many natural ecosystems. Because of their nondegradable nature, heavy metals are a special category of environmental pollutants. They enter ecosystems through a number of anthropogenic activities such as mining, smelting, refining, and electroplating industries. Due to their non-degradable nature, heavy metals accumulate in the soil and sediments and bioaccumulate in the flora and fauna of aquatic ecosystems (Forster and Wase 1997; Chandra et al. 2009; Yadav et al. 2017). Various scientific methods have been investigated for the removal of heavy metals from the contaminated water bodies: physicochemical techniques like chemical oxidation/reduction, electrochemical treatment, precipitation, ion exchange, ultrafiltration, reverse osmosis, and bio-membrane (Ahluwalia and Goyal 2007; Barakat 2011; Saxena et al. 2020). However, these technologies are found to have numerous limitations such as their non-eco-friendly nature, high operational costs, low efficiency, and other concerns (Khoshmanesh et al. 1996; Chong et al. 2000).

Application of living organisms for the removal of toxic metals from contaminated water bodies has been identified as a promising alternative of these physicochemical techniques (Mishra and Bharagava 2016). The use of algae for the remediation of aquatic contaminants from water and wastewater is known as phycoremediation. Along with the removal of toxic metals, it has been observed that algae, especially microalgae, are ideal for sequestration of nitrogen (N) and phosphorus (P) from wastewater because they require these elements as growth nutrients (Mehta and Gaur 2005; Ruiz-Marin et al. 2010; Xin et al. 2010; Pittman et al. 2011; Babu et al. 2018). This chapter highlights the removal of several toxic heavy metals by various algal species and their metal removal potential along with different factors that influence the process. The potential of carbon sequestration and biofuel production as value-added properties of phycoremediation are also discussed in this chapter.

4.2 Sources of Heavy Metals

The origin of heavy metals can be both natural and anthropogenic and have widespread environmental distribution. Natural sources of heavy metals occur through geological and geographical processes like nonuniform formation of parent rock, stratigraphy, topography, weather, erosion, volcanic eruptions, forest fires, aerosol particulates, uptake of metals by plants, subsequent release through decomposition, and other natural sources (Fig. 4.1). In the environment, rocks and soils are the primary natural sources of heavy metals. Hazardous impacts of volcanic eruption affect the environment and health which are exposed to heavy metals. During volcanic eruption, various gases like SO_2, CO_2, and CO, various organic

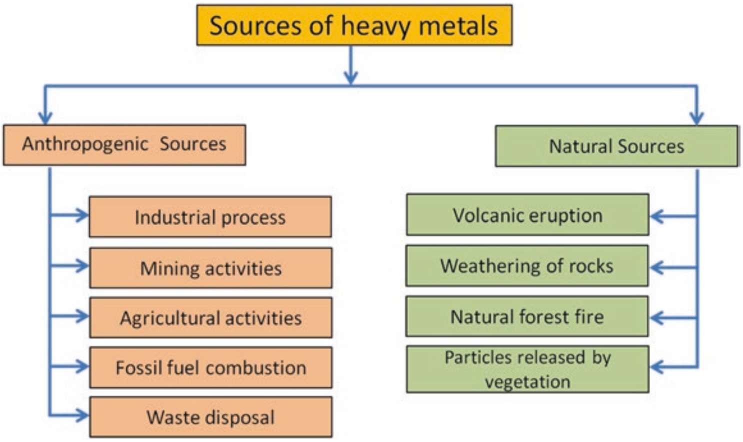

Fig. 4.1 Sources of heavy metals in the environment

compounds (VOCs), and heavy metals like Hg, Pb, Cd, and Au are released into the environment. Various heavy metals enter vegetation through root uptake in the soil or aerial deposition onto leaves and subsequent absorption or drainage into open stomata (Sardar et al. 2013).

Anthropogenic sources of toxic metals include industrial processes; mining and extraction operations; textile activities; landfill leaches; sewage discharge; urban runoff; industrial and municipal wastewater; fossil fuel combustion; wastewater application on agricultural land; application of fertilizers, insecticides, and pesticides; and other human sources (Morais et al. 2012). The main heavy metals found at polluted sites are Cd, As, Cr, Pb, Cu, Zn, Hg, and Ni (Wuana and Okieimen 2011; Bharagava and Mishra 2018).

Arsenic is a naturally occurring metalloid. Arsenic rarely exists as a free element in nature, but rather as a powdery amorphous and crystalline form in ores. The natural sources of arsenic are contributed by weathering of rocks, forest fires, volcanic eruptions, and geothermal waters. Beside natural sources, anthropogenic activities like mining and smelting processes, metallurgical operations and coal combustion, wood preservatives, and use of herbicides and pesticides play an important role in arsenic contamination in the environment (McArthur et al. 2001; Bhattacharyya et al. 2003; Kossoff and Hudson-Edwards 2012; Sailo and Mahanta 2014).

Cadmium finds its way into the environment through natural as well as anthropogenic sources. Natural sources include volcanic eruption, oceanic spray, and forest fires. The key anthropogenic sources of Cd contamination to the environment are coal mining, metal-ore refining, fossil fuel combustion, cadmium-containing pigments, phosphate fertilizers, alloys, electronic compounds, detergents, and rechargeable batteries. Chromium enters the environment naturally by weathering of rocks, oil and coal burning, volcanic eruption, soil and sediments, and anthropogenically enters from sewage, fertilizers, combustion of fossil fuels, manufacturing of plastics, chromate production, and metal electroplating (Mishra and Bharagava 2016). Paper, pulp, and rubber manufacturing, and use of chromium in the leather and tannery industries (Mohan et al. 2006; Saxena et al. 2017), are further anthropogenic sources. A large amount of wastewater is discharged from industries due to extensive use of chromium compounds which contain toxic chromium species.

Lead is a common, abundant, and toxic heavy metal. In the earth's crust, 0.1% by weight lead occurs in rocks and soil. Lead is also found naturally in some plants. Exposure to lead is associated with more than 900 industries, and it accumulates in soil as dust. Anthropogenic sources include mining, smelting, refining, and battery manufacturing (Karrari et al. 2012). Applications in fertilizers and pesticides, sewage sludge application as irrigation from polluted water bodies, effluent discharge from industries to rivers, and coal-based thermal power plants contribute to soil lead pollution (Jalali and Khanlari 2008).

Three forms of mercury exist in nature-elemental (metallic), inorganic salts, and organomercurial compounds. An average of 0.08 mg kg^{-1} Hg is present in the earth's crust and enters the environment from ocean evaporation, weathering of rocks and soils, forest fires, and volcanic gases. Anaerobic bacteria convert soil-bound Hg into dimethyl mercury. Plants take up Pb and release it as mercury vapour during transpiration. Mercury reaches the environment through anthropogenic activities like agriculture, burning of fossil fuels, municipal and industrial wastewater discharge, paper manufacturing, extensive use of the metal in industries, mining, and electrical appliances (Chen et al. 2012).

Naturally, nickel is found in soil and volcanic rock and enters into rivers and other water bodies through leaching of minerals and weathering of rocks and soils. Zinc is an essential element that occurs naturally in soil (approximately 70 mg kg^{-1} in crustal rocks) (Davies and Jones 1998). Zn enters the environment through industrial applications in mining and metallurgical processing of zinc ores and coal burning. Anthropogenic origin of these heavy metals in the soil tends to be more mobile and bioavailable than natural ones (Kuo et al. 1983).Table 4.1 shows the major heavy metals and their different sources.

4.3 Toxicity of Heavy Metals

The most abundant and commonly found heavy metals at contaminated sites are Pb, Hg, As, Cr, Cd, Zn, and Cu (USEPA 1996). Heavy metals are oxidized to carbon (IV) oxide in soil by the action of microorganisms. However, most of the heavy metals are not degraded by chemical or microbial action and their concentrations persist in soil for long periods of time (Adriano 2003). Metal toxicity affects many aquatic bodies as well as water quality criteria, and these problems are exacerbated because metals can transport along with sediments, enter into the environment, and finally bioaccumulate in the food chain. The presence of heavy metals in the soil, air, and water pose a serious threat to humans through skin absorption, contact with contaminated soil, direct ingestion of contaminated foods through bioaccumulation up the food chain, and drinking of contaminated ground water. Heavy metals may come in contact with humans through residential activities (e.g. fertilizers and pesticides),

Table 4.1 Different sources of heavy metals

Metal	Various sources
Aluminium	Cooking utensils, city water supplies, ore smelting plants, anti-perspirants, cosmetics, automotive exhausts, pesticides
Arsenic	Fuel burning, mining, thermal power plants, smelting operations, combustion of coal, production of iron and steel, tobacco smoke, metal foundries, specialty glass products, ore smelting plants, weed killers, pesticides, fungicides, wood preservatives
Cadmium	Waste batteries, e-waste, welding, electroplating, ceramic glazes/enamels, cigarette smoke, food (from cadmium-contaminated soil), tap and well water, pesticides, fungicides, sewage, paints sludge, mines, incinerations and fuel combustion, power and smelting plants, seafood
Chromium	Mines, mineral sources, industrial coolants, chromium salts used in manufacturing, leather tanning, sewage, and fertilizers
Copper	Copper cookware, jewellery, dental alloys, water from copper pipe, mining, electroplating, smelting operations, fungicides, pesticides
Lead	Fuel combustion, lead in industrial processes, gasoline, smelting operations, solid waste combustion, metal plating and finishing operations, used in ceramics and dishware, PVC mini-blinds, coal-based thermal power plants, fertilizers, pesticides
Mercury	Solid waste combustion, mining, smelting, thermal power plants, fluorescent lamps, batteries, thermometers, barometers, dental amalgam fillings, cosmetics, pesticides, insecticides, fungicides, paints, laxatives, fish, shellfish, tap and well water, thermostats, vaccines
Zinc	Metal plating, electroplating, smelting, refineries, plumbing, brass manufacture
Nickel	Thermal power plants, electroplating, smelting, batteries

industrial processes (e.g., manufacturing), pharmaceuticals, and agriculture. Heavy metals enter into human body through ingestion and absorption, and it becomes injurious to human health when their rate of accumulation outnumbers the rate of discharge.

4.3.1 Toxicity of Heavy Metals to Animals

Generally, small amounts of heavy metals are necessary for good health, but prolonged exposure and higher concentrations become toxic or detrimental to human health. Toxicity of heavy metals can cause chronic, degenerative conditions, reduced energy levels, damage vital organs, and lower blood quality. Prolonged exposure of heavy metals can cause physical, muscular, and neurological degenerative problems, cancer-like diseases, and eventually death (Jarup 2003). Examples of health effects of heavy metals and route of entry to the human body are summarized in Table 4.2.

Table 4.2 Route of entry and the health effects of important heavy metals

Metal	Route of entry	Health effects	Symptoms/disease	References
Pb	Inhalation of dust particles or aerosols, consumption of Pb-contaminated food, water, and dermal contact	Higher concentration of the metal may damage the foetus and central nervous system. Lead toxicity harms kidneys, liver, haemoglobin synthesis, endocrine system, reproductive system, irreversible brain damage	Irritability, headache, poor attention span, dullness and memory loss, nausea, insomnia, anorexia, anaemia	NSC (2009); Wuana and Okieimen (2011)
Cr	Inhalation, through the skin	Higher concentrations cause skin ulceration, damage the kidney and affect the central nervous system. Occupational and environmental exposure to Cr (VI)-containing compounds cause asthma, allergy, and cancer	Vomiting, persisting diarrhoea, anaemia, irritation, and ulcers in the stomach	Goyer (2001)
As	Inhalation, ingestion, dermal contact, and the parenteral route to some extent	Carcinogen to skin, lung, bladder, kidney, gastrointestinal damage, birth defects, diarrhoea, severe vomiting, and death	Weakness, skin lesions, sloughing, fever, hypovolemic shock, anorexia, gastrointestinal pain, peripheral vascular disease, pulmonary disease, diabetes mellitus, hypertension, cardiovascular disease, hematemesis, haemolysis, jaundice, proteinuria, haematuria	Tchounwou et al. (1999); Smith et al. (2000)
Zn	Ingestion	Increased cholesterol levels and anaemia	Abdominal pain, lack of muscular coordination, nausea, and vomiting in children	Wuana and Okieimen (2011)
Cd	Inhalation and ingestion	Renal dysfunction, lung cancer, increase blood pressure, oxidative stress, and enzymatic systems of cells	Headaches, weakness, chills, vomiting, nausea, diarrhoea, pulmonary oedema. “Itai-Itai” disease caused by Cd toxicity results in multiple fractures arising from osteomalacia	Murata et al. (1970)

(continued)

Table 4.2 (continued)

Metal	Route of entry	Health effects	Symptoms/disease	References
Cu	Ingestion of Cu-contaminated food	Irritation of stomach and intestine, anaemia, kidney and liver damage, central nervous system damage, and depression	Vomiting, diarrhoea, and loss of strength	Wuana and Okieimen (2011)
Hg	Absorption through skin, inhalation, ingestion, consumption of contaminated aquatic animals	Methyl mercury is highly toxic and harmful to the central nervous system and causes adverse neurological and behavioural changes; DNA damage, brain dysfunction, reproductive effects (i.e. birth defects, miscarriages, and sperm damage)	Symptoms: itching, rashes, redness, skin peeling to the nose and soles of the feet, tension, headaches, sleeplessness, vomiting, irritability, fatigue. Methyl mercury toxicity causes Minamata disease in Japan	Jan et al. (2015)

4.3.2 Toxicity of Heavy Metals to Plants

Plants require trace amounts of certain heavy metals like Zn, Cu, Fe, Mo, Mn, Ni, and Co for their growth, but higher level of these metals may be harmful and toxic to the plants. Forest canopy trees capture the air pollutants that get accumulated on their leaf surface. Concentrations of metals higher than optimum levels adversely affect the plant both directly and indirectly. Some examples of negative impacts caused by heavy metals on plants are inhibition of cytoplasmic enzymes and plant growth by chromium; photosynthesis inhibition by Cu and Hg; inhibition of seed germination and decrease of lipid content by Cd; structural damage of cells due to oxidative stress; decrease of plant growth and reduction of chlorophyll content by Pb; and reduction of seed germination by Ni (Gardea-Torresdey et al. 2005). Indirect effects include affecting microbial activities that affect plant growth and replacement of important nutrients at the cation exchange sites of the plants (Taiz and Zeiger 2002).

In plants, cadmium, lead, and nickel are highly toxic at comparatively lower levels. Cadmium is bio-persistent and has a high residence period. Plants grown in soil contaminated with Cd gradually take up the metal, which accumulate in their tissue. Noticeable symptoms like growth inhibition, chlorosis, root tip browning, and finally death commonly follows due to Cd toxicity. Cd adversely affects enzymatic activities, creating oxidative stress leading to nutritional deficiency in plants (Irfan et al. 2013). High concentration of Cd within plants reduced the nitrate reductase enzyme activity in shoots, resulting in the reduction of nitrate absorption and its transport from roots to shoots.

Most of the lead absorbed from the soil remains in plant roots. Lead toxicity affects plant morphology, growth, and photosynthetic processes and causes abnormal morphology and lignification of cortical parenchyma (Paivoke 1983). High Pb concentrations induce reactive oxygen species (ROS) and damage the lipid membrane, which causes adverse impacts to chlorophyll and inhibits photosynthetic processes and ultimately affects the overall plant development (Najeeb et al. 2014). Production of ROS may also damage nucleic acids and proteins and cause structural damage to cells. Nickel is essential in small doses; however, high concentrations of Ni in soil cause some physiological alterations in plants, chlorosis, and necrosis symptoms (Rahman et al. 2005). Ni toxicity changes water balance, reduces enzyme activity, and decreases chlorophyll content and stomatal conductance in pigeon pea (*Cajanus cajan*).

Chromium toxicity includes inhibition of seed germination, leaf chlorosis, root growth reduction, and reduction in plant biomass. Chlorosis and necrosis symptoms are found due to chromium toxicity in plants (Ghani 2011). Oxidative stress caused by chromium toxicity leads to degradation of photosynthetic pigments in plants. Higher concentration of zinc in soil inhibits plant metabolic activities, resulting in leaf senescence, and retarded root and shoot growth. Toxicity of zinc causes chlorosis in younger leaves, and after prolonged exposure, it extends to older leaves (Ebbs and Kochian 1997).

4.4 Remediation of Heavy Metals from Water and Wastewater

The majority of heavy metals cause adverse impacts on living organisms at very low doses and their remediation from the contaminated sites is a challenging but pivotal task. Several methods have been investigated for detoxification of heavy metals present in aquatic ecosystems. Physicochemical methods include adsorption, filtration, chemical precipitation/coagulation, membrane separation, and solvent extraction (Table 4.3).

Phytoremediation has been popularized for the remediation of toxic substances from the contaminated environment while being environmentally friendly and cost-effective (Bauddh and Singh 2012; Bauddh et al. 2016; Bharagava et al. 2017a, b). Although it is a slow process, it provides several value-added benefits such as carbon and nutrient sequestration, biofuel production, and aesthetic values (Bauddh et al. 2015; Chakravarty et al. 2017; Kumar et al. 2017).

Application of algae for the removal of water contaminants is currently observed in wastewater ecosystems. This process of remediation is termed ‘phycoremediation’ in which micro- or macro-algae are used for the decontamination of wastewater. Phycoremediation is used for the removal of excess nutrients, heavy metals, pesticides, dyes, and metal nanoparticles (Ettajani et al. 2001; Pawlik-Skowronska 2003; Chakravarty et al. 2015; Hultberg et al. 2016; Delgadillo-Mirquez et al. 2016;

Table 4.3 Conventional methods for the removal of heavy metals from contaminated water and wastewater (Volesky 2001; O'Connell et al. 2008; Monteiro et al. 2012)

Name of method	Mechanism	Advantage	Disadvantage
Adsorption	Removal by binding of contaminants on the surface of adsorbents	Applicable to wide range of contaminants	Adsorbent dependent
Membrane filtration	Removing contaminants from water by membrane filtration	No waste as by-product	High cost and difficult maintenance
Ion exchange	Exchange of water contaminants as ions by non-hazardous/beneficial ions	High efficiency	High cost and difficult maintenance
Reverse osmosis	Applied high pressure to contaminants from high concentration towards low concentration	High efficiency	High cost
Electrochemical treatment	Applied electricity to remove the dissolved contaminants	No chemicals required for the process	Expensive

Babu et al. 2018). The wastewater is rich in nutrients that are required for algal growth and development like nitrogen, phosphorous, potassium, and other chemicals (Becker 1994; Dominic et al. 2009; Renuka et al. 2013, 2015; Whitton et al. 2015). The cultivation of algae in wastewater also reduces the cost of biodiesel production that requires significant quantities of water, nutrients, light, and energy for equipment (Gupta et al. 2015, 2016). Several researchers have studied using wastewater as a medium for the cultivation of algae for the production of biofuels (Chevalier et al. 2000; Xin et al. 2010; Park et al. 2010; Zhou et al. 2011; Gupta et al. 2015, 2016), which further reduces the cost of phycoremediation.

4.5 Phycoremediation

Wastewater bears diverse groups of inorganic and organic chemicals that can serve as suitable growth conditions for both micro and macroalgae (Olguí 2003; Cai et al. 2013; Gupta et al. 2016). The use of algae for the decontamination of majority of wastewater has been proved to be very effective by several researchers (Cai et al. 2013; Gupta et al. 2016). Algae-based removal of heavy metals works on two major processes: first is through metabolism-dependent uptake and second is biosorption (i.e. adsorption of metals on the algal cells) (Matagi et al. 1998; Afkar et al. 2010). A number of algal species like *Scenedesmus acutus, Chlorella vulgaris*, *Lemna minor, Nostoc muscorum*, *Phormidium ambiguum*, *Pseudochlorococcum typicum*, *Scenedesmus quadricauda,* and *Spirogyra hyaline* have been found to have excellent abilities to extract toxic metals from water and wastewater (Travieso et al. 1999; Peña-Castro et al. 2004; Kumar and Oommen 2012; Shanab et al. 2012; Dixit and Singh 2014; Singh et al. 2016; Gupta et al. 2017; Samadani et al. 2018).

Samadani et al. (2018) studied the bioaccumulation of Cd in *Chlamydomonas reinhardtii* and an acid-tolerant strain CPCC 121 during 48 h at two different pH conditions. *C. reinhardtii* was found to bear a greater Cd uptake in comparison with the strain CPCC 121. Ajayan et al. (2015) used Scenedesmus sp. for the remediation of Cr, Cu, Pb, and Zn from tannery wastewater. *Scenedesmus* removed Cr by 81.2–96%, Cu by 73.2–98%, Pb by 75–98%, and Zn by 65–98%.

Ajayan et al. (2011) studied the accumulation of Cu, Co, Zn, and Pb by *Scenedesmus bijuga* and *Oscillatoria quadripunctulata* through cultivating them in sewage water and petrochemical effluent. They found that both the species accumulated significant amounts of all the studied heavy metals, and the rate of accumulation from sewage wastewater and petrochemical effluent was 37–50, 20.3–33.3, 34.6–100, and 32.1–100%, respectively, for *O. quadripunctulata* and 60–50, 29.6–66, 15.4–25 and 42.9–50%, respectively, for *S. bijuga*. In a study conducted by Singh et al. (2016), *Lemna minor*, an aquatic plant commonly known as Duckweed, was found to accumulate As up to 735 mg kg^{-1} in its leaves. *Lemna minor* was cultivated in an aquatic area naturally contaminated by As. Kim et al. (2003) evaluated heavy metal (Cu, Cd, Cr, Zn, and Pb) accumulation potential of the brown macroalga *Sargassum horneri*. The metal accumulated was in the order of Zn > Cu > Cr > Pb > Cd. Chen and Pan (2005) examined applicability of the Cyanobacteria genus *Spirulina* for the removal of Pb from wastewater. Adsorption rate of *Spirulina* was found 74% of Pd and the maximum biosorption efficiency of *Spirulina* cells was 0.62 mg Pb per 10^5 algal cells.

The microalga *Scenedesmus incrassatulus* was used to remove three heavy metals (Cu, Cd, and Cr) growing in wastewater (Peña-Castro et al. 2004). Cr and Cd were found to bear significant positive interaction which enhanced the removal of both metals. *S. incrassatulus* efficiently removed the metals by 25–78%. Travieso et al. (1999) studied the effects of Cd, Cr, and Zn on the growth of *Scenedesmus acutus* and *Chlorella vulgaris* and their metal accumulation capacity. Both microalgae had good metal tolerance capacity, allowing these algae to remove higher concentrations of these toxic metals. Maximum Cd, Zn, and Cr removal efficiency of *Chlorella vulgaris* was 38–78% and for *Scenedesmus acutus* was 31–91%. Three microalgae (*Pseudochlorococcum typicum, Phormidium ambiguum*, and *Scenedesmus quadricauda*) were studied for the removal of Hg, Pb, and Cd in aqueous solutions by Shanab et al. (2012). They found that Hg caused severe toxic effects even at low concentration. However, initial concentrations of two other metals (Pb and Cd) increased algal growth. The removal of Hg, Pb, and Cd by *P. typicum* was highest 97% for Hg, followed by 86% for Cd, and 70% for Pb in the first 30 min of contact time. Azizi et al. (2012) used Oscillatoria sp. for biosorption of Cd cultivated in artificial aqueous solution. They observed that this alga has good potential for biosorption of the metal, and various factors influence the biosorption rate.

Kumar and Oommen (2012) used dry biomass of *Spirogyra hyaline* for the removal of five metals Hg, Cd, Pb, As, and Co. The highest amount of metals such as As, Cd, and Hg were removed at lower metal concentrations (i.e. 40 mg L^{-1}); however, Co and Pb exhibited the highest removal at 80 mg L^{-1}. The metal adsorption by dry biomass was found in order of Hg > Pb > Cd > As > Co. In a study conducted by Rehman and Shakoori (2004), *Chlorella* sp. found to have substantial tolerance against Cd at the concentration of 10 mg/mL and Ni at the concentration of 12 mg mL^{-1}. Chlorella removed significant amounts of both the metals. The reduction of Cd after 28 days from solution was up to 96%, and in the reduction of Ni from the medium after 28 days was 94%. *Tetraselmis suecica* and *Skeletonema costatum* were found to be hyperaccumulators of Cd (Ettajani et al. 2001). Zhou et al. (2012) studied Zn and Cu removal potential by two marine algae *Chlorella pyrenoidosa* and *Scenedesmus obliquus*. Both the species were found to bear approximately 100% metal removal ability. The applications of algal species in the removal of various heavy metals are shown in Table 4.4.

4.5.1 Factors Influencing Phycoremediation

Removal of toxic metals by using algae is a natural and cost-effective technique, and it depends on several factors like type and level of contaminants, algal species, algal biomass, temperature, pH, presence of nutrients, and other factors (Selatina et al. 2004; Murugesan et al. 2006; Zeraatkar et al. 2016; Samadani et al. 2018). Biological factors like interspecies competition and presence of microorganisms (bacteria, viruses, and fungi) influence the growth of the phycoremediator algal species and may create noticeable limiting parameters (Grobbelaar 2000; González-Fernández et al. 2011).

4.5.1.1 Effect of pH

Among various factors that can influence the biosorption of metal ions, pH of the solution is a pivotal parameter (Matheickal and Yu 1996; Selatina et al. 2004; Samadani et al. 2018). pH alters the properties of the growing medium, metal binding sites of the sorbents, as well as properties of the metal ions (Esposito et al. 2001; Selatina et al. 2004; Vijayaraghavan and Yun 2008; Monteiro et al. 2012). Several studies reported that metal removal rate is enhanced with increased pH, while decreased pH values reduce the metal sorption efficiency of algal species (Mehta and Gaur 2001; Chojnacka et al. 2005; Gupta et al. 2006; Doshi et al. 2007; Liping et al. 2008; Abdel-Aty et al. 2013; Li et al. 2017). Sheng et al. (2004) reported that optimum pH for highest biosorption for Pb and Cu is 5.0 and for Cd, Zn, and Ni is pH 5.5 for marine algae *Padina* sp., *Gracilaria* sp., *Sargassum* sp., and *Ulva* sp.

Many researchers have observed that increased pH (5.0–6.0) reduces electrostatic repulsions between the adsorbents' surface and metals, resulting in increased metal removal by the algae (Ibrahim 2011; Momcilovic et al. 2011; Hassan et al. 2014). Samadani et al. (2018) studied phycoremediation potential of two algal species (*Chlamydomonas reinhardtii* and CPCC 121, an acid-tolerant strain) in two pH conditions (pH 4 and pH 7). At pH 7, Cd removal ability of *C. reinhardtii* was found

Table 4.4 Application of several algal species for the removal of heavy metal

Algal species	Metal(s)	Medium of cultivation	References
Scenedesmus acutus and *Chlorella vulgaris*	Cd, Zn, and Cr	Synthetic growth medium	Travieso et al. (1999)
Nostoc rivularis and *N. linckia*	Cd and Zn	Sewage water	El-Enany and Issa (2000)
Sargassum horneri	Cu, Cd, Cr, Zn, and Pb	Natural coast	Kim et al. (2003)
Scenedesmus incrassatulus	Cr, Cd, and Cu	Artificial wastewater	Peña-Castro et al. (2004)
Chlorella sp.	Cd and Ni	Synthetic growth medium	Rehman and Shakoori (2004)
Anabaena subcylindrica and *Nostoc muscorum*	Cu, Mn, Co, and Pb	Industrial wastewater and Sewage	El-Sheekh et al. (2003)
Spirulina sps	Pb	Synthetic growth medium	Chen and Pan (2005)
Cladophora fascicularis	Pb and Cu	Aqueous solution	Liping et al. (2008)
Scenedesmus bijuga and *Oscillatoria quadripunctulata*	Cu, Co, Pb, Zn	Sewage water	Ajayan et al. (2011)
Caulerpa racemosa and *Sargassum wightii*	Cr, Pb, and Cd	Aqueous solution	Tamilselvan et al. (2012)
Oscillatoria sp.	Cd	Artificial aqueous solution	Azizi et al. (2012)
Spirogyra hyalina	Cd, Hg, P, As, and Co	Artificial aqueous solution	Kumar and Oommen (2012)
Ulva lactuca	Cd	Artificial aqueous solution	Lupea et al. (2012)
Pseudochlorococcum typicum, Phormidium ambiguum, and *Scenedesmus quadricauda*	Hg, Pb, and Cd	Artificial aqueous solution	Shanab et al. (2012)
Chlorella pyrenoidosa and *Scenedesmus obliquus*	Zn and Cu	Artificial aqueous solution	Zhou et al. (2012)
Nostoc muscorum	Cd and Pb	Metal solution	Dixit and Singh (2014)
Spirulina platensis	Cd	Artificial aqueous solution	Al-Homaidan et al. (2015)
Scenedesmus sp.	Cr, CU, Pb, and Zn	Tannery wastewater	Ajayan et al. (2015)
Lemna minor	As	Natural contaminated area	Singh et al. (2016)
Chlamydomonas reinhardtii	Cd	Artificial aqueous solution	Samadani et al. (2018)

to be limited due to its toxicity that was also dependent on exposure time and concentration of the metal in the growing medium. Rangsayatorn et al. (2004) reported insignificant removal of Cd by *Spirulina platensis* at pH 3.0; however, at higher pH up to 8.0, Cd adsorption increased substantially.

4.5.1.2 Effect of Temperature

Temperature of the medium is also an important limiting factor for the removal of metal contaminants of the aquatic ecosystems. Temperature may alter the metal removal potential of algal species and the chemistry of heavy metals. Higher temperature increased metal-binding ability of algae by enhancing surface activity as well as kinetic energy of the contaminants (Skowronski 1986; Sag and Kutsal 2000; Mehta et al. 2002; Vijayaraghavan and Yun 2007). Few studies indicate that the sorption of metal ions reduced with increased temperature (Suhasini et al. 1999; Benquell and Benaissa 2002; Sari et al. 2007; Herrero et al. 2008).

4.5.1.3 Effect of Contact Time

Heavy metal removal efficiency of algal biomass is influenced by contact time (Murugesan et al. 2006; Aroua et al. 2008; Wu et al. 2008; Saif et al. 2012). Ibrahim (2011) observed that *Ulva lactuca* and its activated carbon have maximum sorption capacity at a contact time of 60 min for Cd, Cr, Pb, and Cu ions. They also reported that after 60 min the adsorption rate was almost constant. Abdel-Aty et al. (2013) studied the impact of contact time on removal of Pb and Cd by *Anabaena sphaerica*. They found that the biosorption of the metals was faster in the initial 20 min, and after that it was gradually increased up to 60 and 90 min for Cd and Pb, respectively. Chen et al. (2008) reported a similar trend of Ni and Cu removal by *Undaria pinnatifida* and contact time.

4.5.1.4 Effect of Biomass Concentration

In phycoremediation, biomass concentration has been found to be a strong metal biosorption-influencing factor (Nuhoglu et al. 2002; Gong et al. 2005; Karthikeyan et al. 2007; Sari and Tuzen 2008; Abdel-Aty et al. 2013). Increased biomass in the growing medium adversely influences the biosorption (Hamdy 2000; Nuhoglu et al. 2002; Gong et al. 2005). This is probably due to the aggregate's formation of the biosorbent at higher biomass that decreases the surface area of the biosorbents (Karthikeyan et al. 2007; Sari and Tuzen 2008). Abdel-Aty et al. (2013) found that the biosorption of Pb and Cd by *Anabaena sphaerica* was enhanced by increasing biosorbent and became constant at higher dosage from 0.1 g 100 mL^{-1} for Pb and 0.2 g 100 mL^{-1} for Cd. Al-Homaidan et al. (2015) reported that the biosorption efficiency of *Spirulina platensis* for Cd increases with higher biomass from 0.25 to 2 g; however, at 1.75 and 2 g doses, no substantial change occurred during the study. Solisio et al. (2008) observed that the dose of 2.0 g of *Spirulina platensis* is sufficient for the removal of Cd up to 98%.

4.5.1.5 Effect of Metal Ion Concentration

The removal of metal ions basically depends on the concentration of metal present in the medium (Saleem and Bhatti 2011; Al-Homaidan et al. 2015). Generally, the biosorption of metal ions increases if the metal concentration in the medium increases, but this is up to a certain limit, and thereafter, the biosorption may be saturated or decreased (Aloysius et al. 1999; Saleem and Bhatti 2011; Lupea et al. 2012; Al-Homaidan et al. 2015). Biosorption of Cd by *Ulva lactuca* increased at metal concentration from 22.53 to 540.62 mg L^{-1}; however, Cd removal decreased from 80.78 to 42.43% at higher doses of the metal (Lupea et al. 2012). Ibrahim (2011) reported that the biosorption of Cu, Cr, Cd, and Pb by *Ulva lactuca* increased in the beginning and achieved maximum removal by 87.5% at 60 mg L^{-1}. After this dose of metal ions, the rate of adsorption was largely unchanged. Further increased metal level decreased the adsorption process.

4.6 Carbon Sequestration Potential of Algae

Climate change is a serious global issue. Some debate that it is caused by various natural internal or external processes, but the majority of credible scientists that the main driver of global climate change (GCC) is anthropogenic. CO_2 is the chief greenhouse gas (GHG), and its sequestration through algae is an important tool for mitigation of GHG (Eloka-Eboka and Inambao 2017). Although the global warming potential of CO_2 is lower than methane (CH_3), increased sources emitting CO_2 is what makes it the most serious GHG. The option of sequestering CO_2 naturally through biological means is attractive because plants naturally capture CO_2 through photosynthesis (Maraskolhe et al. 2012). Carbon capture along with bioenergy production (creating biofuel through algal oils) can play a pivotal role for CO_2 mitigation (Moreira and Pires 2016).

In aquatic ecosystems, both macro- and microalgae play a significant role in capturing carbon. The carbon is sequestered by these algal species in the form of bicarbonates (HCO_3) or CO_2. Carbon is the basic constituent of all organic molecules. Accumulated stored oils can be harvested to produce bioethanol, biodiesel, polyunsaturated fatty acids, and other bio-products (Spolaore et al. 2006; Milledge 2011; Razzak et al. 2013; Klinthong et al. 2015).

Different species of algae have different tolerance levels for CO_2. Ono and Cuello (2003) found that *Cyanidium caldarium* was the most CO_2-tolerant species they studied. However, several other species like *Scenedesmus* sp., *Chlorococcum* *littorale, Synechococcus elongatus,* and *Euglena gracilis* have also been found to have good tolerance levels (60–80%).

Creating a huge carbon sink would require large areas of aquatic habitat as well as large capital expense. The use of algae has been seen as an economical and feasible solution in this regard. Microalgae are more photosynthetically efficient than terrestrial plants because they have greater access to nutrients, water, and CO_2 and can thus more efficiently convert solar energy into biomass (Maraskolhe et al. 2012). It has been estimated that about 173 Tg C year^{-1} of CO_2 could be globally sequestered by macroalgae. They can fix CO_2 from various sources like industrial exhaust, soluble carbonate salts, and other sources. Generally used microalgae include Chlorophyceae (green algae), Cyanophyceae (blue-green algae, which are actually photosynthetic bacteria), Bacillariophyceae (diatoms), and Chrysophyceae (golden algae).

The carbon sequestration potential of algae can be further enhanced by manipulating key enzymes through genetic engineering (Bajhaiy et al. 2017). The amount of CO_2 fixation plays an important role in affecting various metabolic processes of the cell including carbohydrate, lipid, and biomass synthesis (Wang et al. 2008). One of the advantages associated with capturing carbon in aquatic habitats is the efficiency to sequester CO_2 in the non-gaseous form of bicarbonates that fertilizes algal growth. At pH ≥ 7 and temperature <30 °C, bicarbonate is the dominant form of CO_2 in water. Algae have active pumps for bicarbonate, and they have the ability to concentrate bicarbonates into their cell. This bicarbonate is then dehydrated, either by carbonic anhydrase or spontaneously, resulting in CO_2 trapped by the Calvin cycle. 1.6–2.0 g of CO_2 can be trapped per gram of algae biomass (Herzog and Golomb 2004).

Flue gas emitted from fossil fuel power plants has high emissions of CO_2 along with SOx and NOx gases. When this flue gas is injected into algal ponds, it increases algal biomass yield by almost threefold, but this requires a large amount of energy (Jeong et al. 2003). There are multiple factors that influence CO_2 sequestration, such as pH, temperature, oxides of sulphur (SOx), and oxides of nitrogen (NOx) in the flue gas, light, and other factors. It can be concluded that algae have a high carbon sequestration potential provided there are optimum conditions.

4.7 Bioenergy Production by Algae

Demand for energy has seen an unprecedented rise in the recent past, resulting in increased consumption of fossil fuel. There is still a sufficient supply of fossil fuel available economically, but using fossil fuel at this rapid rate is not safe for longer periods of time mainly due to rising GHG emissions. GHGs pose a severe impact on the environment through contributions to GCG. Therefore, there is a dire need to identify alternative sources of renewable energy that are economical as well as carbon neutral (Voloshin et al. 2016).

Biofuels are available for usage at a commercial scale such as bioethanol obtained from corn starch or sugarcane and biodiesel from oil crops, but crop-based biofuels raise critical ‘food versus fuel’ impacts on society (Demirbas 2009; Pittman et al. 2011). The advantages of using microalgae to sequester CO_2 and provide biofuel and other by-products is that they are not considered a ‘food’ crop for humans, they grow rapidly, and different species can be grown in saltwater, freshwater, and in polluted sewage and industrial water.

There are a number of advantages of using biodiesel produced from algae, including it does not have sulphur content; it is a ‘drop-in’ fuel (i.e. its chemical composition is quite similar to fossil fuel gasoline and can thus be used with little modification in internal combustion engines); and it generates less CO, SOx, NOx, and hydrocarbons emissions than combusting fossil fuels (Tokusoglu and Una 2003). Thus, biofuels obtained from cultivation of algae provides an alternative fuel that does not negatively affect agriculture. Algae like *Scenedesmus, Botryococcus,* and *Chlorella* have been tested for the production of biodiesel (Wang et al. 2013; Nascimento et al. 2013). Currently, researchers are focussing on maximizing the biodiesel yield from suitable species of algae, and much research and development is being done to increase the biodiesel production through cheaper and more effective technology. Biodiesel feedstock obtained from plants like Jatropha and Karanja needs to be pre-treated before production of biodiesel, which is not required for algae, which is yet another advantage (Delucchi 2003).

Wastewater proves to be an encouraging resource for the cultivation of microalgae (Chen et al. 2015). Combining cultivation of microalgae with treatment of wastewater (Fig. 4.2) can help in reducing CO_2 emissions, reduce nutrient pollution, and lowering the cost of biofuel production through not having to add fertilizer to enhance algal growth.

Some species of algae can accumulate high amount of lipids (Table 4.5) within their cells that may be exploited as feedstock for producing biodiesel, but intensive research is required to support this potential and optimize the systems of cultivation and harvesting of biomass (Simionato et al. 2013; Kumar et al. 2015). Production of biodiesel by lipid extracted from microalgae can be coupled with other energy processes that can make biodiesel a sustainable and economical product (Ansari et al. 2017).

Microalgal biotechnology shows a way forward as it can increase lipid and biomass productivity. Despite tremendous potential, traditional approaches are in dire need of improvement for increased lipid accumulation, so that they can be used for commercialization of biodiesel (Ravindran et al. 2017). However, production of biofuel has received a lot of attention currently, and it has the potential to replace the fossil fuels (Milano et al. 2016). Despite algae being considered as an alternative fuel, they are yet to attain techno-economic sustainability. Currently, the production of algal biofuel is costly (Lundquist et al. 2010). Biomass production faces a few technical issues with biomass production, processing of lipids, production of biofuel, and harvesting (Shriwastav and Gupta 2017).

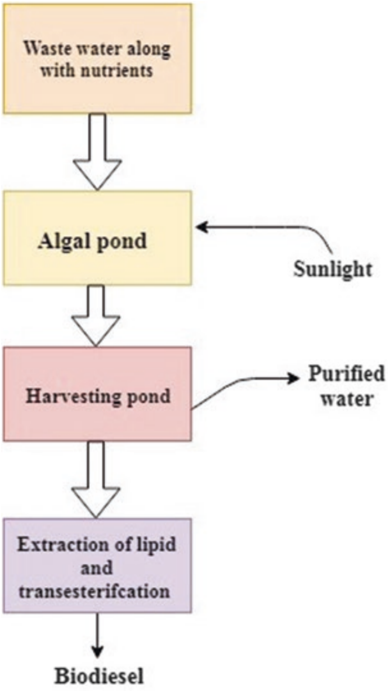

Fig. 4.2 A flowchart illustrating the production of biodiesel from algae in wastewater systems

Table 4.5 The lipid content of some microalgae (Gouveia and Oliveira 2009)

Species	Lipids (% dry matter)
Spirulina maxima	4–9
Chlorella minutissima	57
Dunaliella salina	14–20
Chlorella vulgaris	14–40/56
Chlorella emersonii	63
Chlorella sorokiniana	22
Dunaliella bioculata	8
Neochloris oleoabundans	3565
Scenedesmus obliquus	11–22/35–55
Chlorella protothecoides	23/55
Scenedesmus dimorphus	6–7/16–40

4.8 Conclusion

Toxic metal contamination of aquatic habitats is a severe environmental issue. Remediation of these contaminants through environmentally friendly technologies is a challenging task. Phycoremediation, especially of heavy metals, has emerged as a promising method that can synergistically remediate global environmental pollution through removing toxic metals along with other water contaminants like nutrients, dyes, pesticides, and metal nanoparticles; and coupling phycoremediation of contaminated water and wastewater with bioenergy production. Continued research advancements will hopefully remove the toxic heavy metals from contaminated water and wastewater by algae feasible and attractive for at commercial scale biodiesel production.

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Chapter 5
Advances in Plant–Microbe-Based Remediation Approaches for Environmental Cleanup

Sanjeev Kumar, Nisha Kumari, Susmita Karmakar, Ankit, Ritu Singh, Monalisha Behera, Anita Rani, and Narendra Kumar

Abstract In the present era, one of the most concerning issues is environmental contamination which is endangering human health and the ecosystem, thus the identification and proper implementation of suitable technologies for remediation of contaminated sites is a prerequisite for sustainable development. In this context, several methods have been developed for the mitigation of the adverse impacts of toxic/hazardous contaminants. In the past decade, lot of research have been focused over improving the performance of established remedial technologies with the objective of eliminating the drawbacks and reducing the contaminant concentration to acceptable limits. Plant–microbe interaction has not been extensively studied in agriculture field only but another area in which the partnerships of plants and microbes have been explored is environmental cleanup. Plant–microbe interaction has been found to be a promising approach for in situ remediation of various organic/inorganic pollutants. It offers several ecological and cost-associated benefits. Plant–microbe-assisted phytoremediation could be improved further through genetically modified plants and microbes. The present chapter reviews the role of plant–microbe partnership in removal/detoxification/degradation of different category of contaminants. Additionally, the advancements made in microbe-assisted phytoremediation through the use of transgenic recombinants and integrated nanotechnology are also discussed.

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5.1 Environmental Pollution and Its Effect on Organisms: An Overview

Our earth is getting progressively polluted with different types of inorganic and organic compounds, primarily as a result of anthropogenic activities (Kumar et al. 2017a, 2019). Natural resources (soil, air, and water) have faced a tremendous amount of pressure because of the rising human population and their associated activities. Uncontrolled discharge of effluent from industries in water led to a rapid increase in effluent concentration which alters the nature of ecosystem and adversely affects the health of human beings, plant, and animals (Kumar et al. 2014, 2019; Yadav et al. 2019). There are several ways by which huge amount of toxic compounds enter into the environment.

Industrial processing, facilities for sewage as well as waste water detoxification, accidental oil and chemical spillage, mining processes, military operations, and mobile sources are the pathways for wide range of contaminants through which they enter into different environmental matrices (Kumar et al. 2013, 2014, 2015, 2018a; Singh and Chandra 2019). After getting into the environment, the contaminants can be consumed or inhaled or absorbed by primary consumers that sequentially enter the food chain and get bioaccumulated and then biomagnified at successive trophic levels (Ghavri et al. 2013; Ren et al. 2017). If the adulterants enter the sediments, they could potentially affect the costal bodies and larger water bodies which in turn can have adverse impact on human health (Singh and Chandra 2019). There are some naturally occurring contaminants whose availability and mobility towards food chain may be enhanced due to human activity (Ren et al. 2017).

Contaminants including a wide range of various heavy metals, polyaromatic hydrocarbons (PAHs), persistent organic pollutants (POPs), and polychlorinated biphenyls (PCBs) have already been proven to remain in food chain (Ren et al. 2017; Yadav et al. 2016a, El-Shahawi et al. 2010). Among several toxic contaminants, heavy metal or metalloid, and organic pollutant pose serious threat to plants and animals including humans (Kumar et al. 2014, 2015; Cherian and Oliveira 2005; Yadav et al. 2016b, 2017; Mishra et al. 2018). Heavy metal toxicity in environment is considerably higher due to mining activities (Shahid et al. 2015). Common heavy metals including lead, arsenic, chromium, nickel, zinc, manganese, mercury, aluminum, cadmium, and cobalt occur naturally. As per USEPA (2004) and ATSDR (2012), lead, arsenic, cadmium, and mercury are considered as most significant among top major 20 hazardous adulterants. Human beings are being exposed to the risk of heavy metal toxicity through the uptake of contaminated vegetables, cereals, and pulses (Kumar et al. 2014, 2015; Pierart et al. 2015; Xiong et al. 2016). A lot of serious health disorders viz., nervous system impairment, anemia, cancer, kidney dysfunctions, cognitive impairment, and damage of brain, etc. have been documented as a result of heavy metal toxicity (Jarup 2003).

Generally, inorganic contaminants remain persistent in nature and could pose genotoxic, carcinogenic, mutagenic, and teratogenic effects even at low concentration (Saxena et al. 2019). They also act as endocrine disruptors and persuade developmental as well as neurological disorders, and hence their removal from environment is of prime importance for the betterment of the human society (Saxena et al. 2019). On the other hand, organic pollutants are mostly human generated and have been widely used as industrial solvents, fuel components, and intermediates. Lots of manufactured products such as paints, adhesives, gasoline, and plastics contain harmful organic compounds (Collins et al. 2002; Chandra et al. 2011). Organic compounds like PCBs, TCE, PCE, chloroform, etc. are carcinogenic and neurotoxic in nature (Männistö et al. 2001). Pesticides like atrazine, 2-4 dichloroethane, and hexachlorocyclohexane which are widely used in both agriculture and forestry for pest control have also been reported to have carcinogenic and mutagenic properties (Mauriz et al. 2006).

Soil is the basic requirement for agricultural framework, food security, and environmental sustainability. However, rapid rate of urbanization and imprudent industrialization have rendered this utmost valuable resource contaminated with organic pollutants and heavy metals, debilitating the soil quality, human well-being, and biological systems (Kumar et al. 2017a, 2019). Soil ecosystem degradation may emerge due to buildup of excess heavy metals and organic contaminants within soil. Persistence of the toxicants within soil system is greatly influenced by physical and chemical soil characteristics (Kumar et al. 2018b). Microbial and enzymatic activities within soil may also be hampered due to the accumulation of heavy metals (Kumar et al. 2018b). So, it is indispensable to create an efficient and environment friendly technique to remediate the contaminated soil (Oh et al. 2014). In this regard, several conventional methods like soil excavation and landfilling, soil washing, immobilization, or extraction by physicochemical techniques have been used to clean up the environment, but most of them are costly and require high capital investment.

In recent times, various remedial techniques have been evolved and successfully deployed for environmental cleanup (Kumari et al. 2016; Sabir et al. 2015; Verbruggen et al. 2009). These methods are helpful to ameliorate the available fraction of contaminants within environment as well as can subsequently diminish the rate of bioaccumulation and bio-magnification of environmental contaminants in successive trophic levels (Bhargava et al. 2012). One of these methods that represents an eco-friendly, cost-effective, and eco-sustainable alternative to the conventional methods of treatment is phytoremediation (Pilon-Smits 2005). Certain plants are capable of accumulating inorganic pollutants in their root and shoot systems while degrading the organic pollutants in the surrounding zones. Plant–microbe interaction plays a key role in enhancing the efficiency of phytoremediation in degrading pollutants. Plant–microbe partnership has improved the remediation process to a quite great extent.

Introducing nanotechnology in the transgenic plants is like cherry on the cake. When both these technologies are combined, the contaminants get removed effectively consuming less time and posing no harmful threats on the environment. The present chapter gives a brief overview of existing remedial techniques followed by detailed description of role of plant–microbe partnership in plant-assisted remediation. Further, the impression of transgenic plants and nanotechnology in boosting phytoremediation capacities of plants has been discussed.

5.2 Remediation Strategies for Environmental Cleanup

A systematic approach is required for effective cleanup of contaminated soil and/or ground water. An appropriate remedial action is selected on the basis of contaminants' concentration and the risk to environment likely to be emerged from the consequence of contamination. Site characterization and risk assessment are two important tasks to be done prior to the selection of a particular remedial measure. Both of these actions confirm the actual toxic level of contaminants at a particular environment and their probable risk to environment and human well-being. Depending on the existing risk, suitable remediation strategies are developed. Although remedial measures could not result in absolute cleanup of the contaminated area, however these actions potentially curtail the contaminants' concentration to match the regulatory considerations. This can be achieved through limiting the downward movement of toxicants and/or expelling them. Remediation strategies can be categorized as physicochemical, biological, electro-kinetic, and thermal approaches which are discussed briefly in the following sections.

5.3 Physicochemical Approaches

5.3.1 Replacement and Treatment of Contaminated Soil

This is the simplest technique. The process includes the removal of contaminated soil, disposal of the same, and restoring the area with fresh soil. The evacuated contaminated soil is disposed to landfill site and/or often subjected to soil washing. This approach is apt when the contaminated area is very small (Asquith and Geary 2011).

5.3.2 Soil Washing

This method is appropriate for the soil having inorganic, organic, and radioactive contaminants and lower amount of clay content. If clay content is higher in soil, then a dispersion material is added to break them into fine particles prior to chemical washing of the contaminants. For organic contaminants, a surfactant can be added as a washing agent. During ex situ remediation, the solvent and contaminated soil are mixed up in an extractor vessel (Pavel and Gavrilescu 2008; Balba et al. 1998). The solute and the solvent are treated after separation. Efficiency of the method is increased by using hot water (Wood 2002). It is often applied as a pretreatment approach for soil remediation. In case of in situ soil washing method, solvent or water including additives are injected within the contaminated soil which washes the contaminants. The additives are used for easy release of contaminants.

5.3.3 Solidification and Stabilization

Solidification and stabilization are a source control remediation measure and have already been applied at nearly about 160 superfund sites (Dadrasnia et al. 2013). The process involves the immobilization of toxic contaminants. It can be performed by two ways either through mixing the contaminated soil with a particular additive to make it immobile and insoluble or the contaminated soil converted to insoluble and nonreactive mass prior to solidification. Soil physicochemical characteristics can significantly influence in situ solidification and stabilization action. The ex situ technique includes grinding, dispersing, mixing up with binder material, and disposing off in a landfill. Fly ash, lime, clay, and cement can be used as inorganic binder while resins and bitumen are examples of organic binders (Sun et al. 2016). This method is applicable for remediation of organics, inorganics, semi-volatile, and radioactive contaminants.

5.3.4 Vacuum Extraction

This is a cost-effective in situ remediation measure. Soil and/or ground water contaminated with volatile and semi-volatile organic elements are effectively remediated through vacuum extraction technique. The outline of vacuum extraction technique is shown in Fig. 5.1. The extraction well is fixed at vadose zone (soil water zone). The contaminated soil water and/or volatile compounds are extracted by an injecting medium. Oxygen and nitrogen are commonly used as injecting medium (Reddi and Inyang 2000). Aerobic biodegradation is increased with the use of oxygen as injecting medium. Soil structure and properties of volatile organic components often affect the extraction method. Vacuum extraction is often called as air sparging when air is injected underneath the water table to restore the contaminated groundwater.

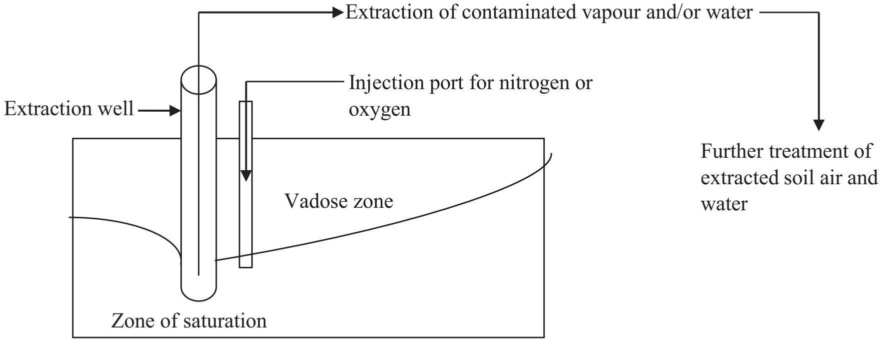

Fig. 5.1 Vacuum extraction technique

5.3.5 Chemical Decontamination

This method is performed to treat the soil having higher concentration of inorganic heavy metals. Selection of extractants is important for sequential extraction of heavy metals from contaminated soil. Oxidizing and reducing agents, electrolytes, acids, etc. can be used as extractants depending upon the heavy metal concentration and soil characteristics. Reduction in heavy metal mobility within the contaminated soil can also be done by introducing immobilizing agents, viz. zeolites, minerals, industrial residues, etc. (Anoduadi et al. 2009). After reducing the mobility of the metals within the soil, contaminated soil can be encapsulated in solid blocks and disposed off to a landfill (Ucaroglu and Talinli 2012). Some additives like concrete, asphalt, or lime are mixed up with the contaminated soil to encapsulate it.

Lime and concrete are applied to the soil having higher oil and heavy metal concentration while, for hydrocarbon contamination, asphalt coating is generally used (Khalid et al. 2017). Now, silica-based coating of contaminated soil is also popularized as it contains various carboxylic groups which act as effective adsorbent for metal ions (Kuang et al. 2015). Sometimes, permeable reactive barriers are used to decontaminate the ground water. Through the process of adsorption, complexation, and precipitation reaction, the inorganic heavy metals are retained in the packing materials of permeable reactive barriers. Most common materials used in permeable reactive barriers are activated carbon, ferric oxides, resins, zeolites, etc.

5.3.6 Electro-Kinetic Method

Electro-kinetic approach is an emerging popular technique to clean up a contaminated soil especially granular soil through electrical principles. An electric field is established within contaminated soil-water system by inserting two electrodes within it. Low direct electric current is applied which results in ion migration and electro-osmosis. Based on the charges, the ionic contaminants are transported to electrodes which are recovered later (Alshawabkeh 2009). Often complexing agents are used to enhance the movements of toxicants. Heavy metals like mercury and uranium contaminants in soil are recovered commercially through electrokinetic method.

5.3.7 Thermal Methods

Thermal remedial techniques are applicable for the contaminants having higher volatilization potential (Evangelou 1998). In case of thermal desorption process, contaminated soil is heated up at 200–1000 °F temperature to separate the contaminants physically from the soil. Most of the contaminants become vaporized during thermal desorption. To decontaminate the remaining toxic elements, secondary treatment techniques like re-ignition, condensation, catalytic oxidation, etc. are used. This method is often applied for petroleum contaminated area. Thermal stripping is also used for treating the volatile and semi-volatile contaminants. Often hot water is injected within contaminated soil matrix to enhance the volatilization potentiality of the contaminants.

High temperature is required for incineration. Incineration can break down the toxic components to basic components like hydrogen, nitrogen, and carbon which react with oxygen to form water, nitrogen oxides, and carbon dioxide. Evaporative loss of volatile compounds during incineration process sometimes makes it inappropriate (Ezeji et al. 2007). Moreover, it is a costly measure requiring larger area for completing the entire process, and it poses threats to environment by emitting pollutants (Bassam and Battikhi 2005).

5.3.8 Biological Methods

Biological treatments are often applicable for the remediation of organic contaminants present in the soil. Bioaugmentation, biostimulation, biofilters, bioventing, bioreactors, and phytoremediation are most commonly applied biological approach to remediate contaminated soil. These biological techniques can be ex situ or in situ in nature. Examples of ex situ bioremediation approaches include anaerobic digestion, land farming, bioreactors, composting, biosorption, etc. Biostimulation, bioventing, and phytoremediation are examples of in situ bioremediation (Table 5.1).

5.3.8.1 Bioremediation

Bioremediation is one of the feasible and eco-friendly ways to remediate or degrade the pollutant with the help of microorganisms (Bharagava et al. 2017; Chowdhary et al. 2017). Bacteria, fungi, and many types of organisms are found to successfully

Table 5.1 Some remediation strategies for environmental cleanup

Remediation strategies	Explanation	References
Bioremediation **Ex situ**—Biopile, windrow, bioreactor, land farming, composting **In situ**—Bioventing, bioslurping	Encourage the development of microorganisms in the contaminated region for degradation/remediation of target pollutants	Azubuike et al. (2016); Sharma et al. (2019)
Phytoremediation	For the direct use of living green plants for remediation of pollutant in soil, mud, sediment, sludge, surface water and groundwater	Yadav et al. (2018); Ashraf et al. (2019)

degrade the complex form to the simpler forms and incorporating the breakdown products into their metabolism. This process is divided into two types. One is ex situ bioremediation wherein the contaminated material is removed from the contaminated sites and bioremediation process is started off site, for example, biopile, windrow, bioreactor, land farming, and composting. Another is in situ bioremediation wherein bioremediation is initiated in the contaminated zone itself, for example, bio-venting and bio-slurping (Sharma et al. 2019; Azubuike et al. 2016).

Bioremediation process has been used in number of contaminated sites of developed and developing countries (Verma and Kuila 2019; Ying and Wei 2019), which showed variable mark of success. Some of the specific requirements of bioremediation include (1) the condition of contaminated area should be suitable for growth and metabolism of microbial population and (2) the availability of the contaminants should be enough for the growth of microbial population. The environmental factors such as soil types and texture, temperature, pH and EC, moisture content, and the presence of oxygen and nutrients play an important role in the degradation of pollutant by the help of microorganisms.

5.3.8.2 Phytoremediation

In 1991, the word phytoremediation has been introduced which is derived from two words “phyto” means plant and “remediation” means recovery. Phytoremediation is a green technology in which plants (hyperaccumulators) and their associated microbes are used to remediate the contaminated site to safeguard the environment (Saxena et al. 2019). It has great remedial potential especially for those pollutants which remains close to the roots of the plant. Over and above, phytoremediation is an economical tool, as it requires less energy as well as an esthetically pleasing technique for remediating polluted sites (Mojiri et al. 2013).

The process of phytoremediation has several mechanisms through which plants accumulate, translocate, and degrade the toxicants like metals, hydrocarbons, pesticides, and chlorinated solvents (Fig. 5.2). This process mainly includes five mechanisms which are as follows:

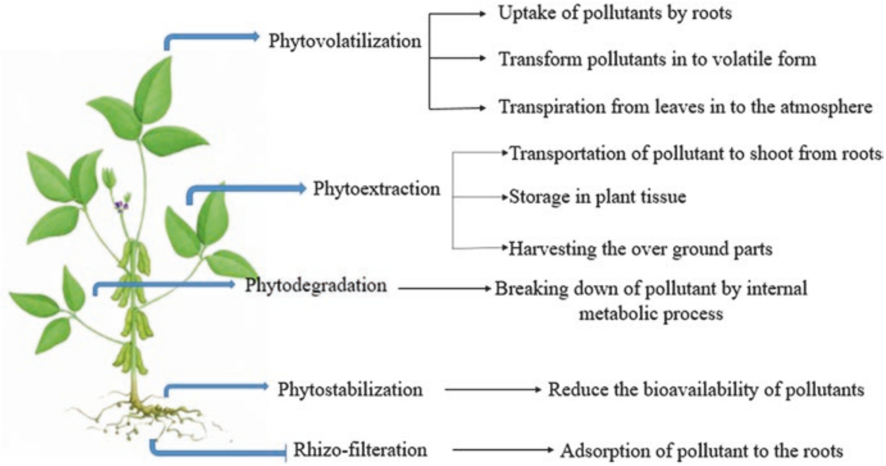

Fig. 5.2 Phytoremediation processes and their mechanisms

(a) **Phytoextraction/Phytoaccumulation:** pollutants in soil, groundwater can be taken up inside plant tissues and accumulated in different plant parts.
(b) **Phytostabilization:** restricts the migration of contaminants in soil and also reduces the bioavailability of pollutants.
(c) **Phytodegradation:** mainly degrades aromatic pollutant (carbon tetrachloride, hexachloroethane, DDT, etc.) by the microorganism in the root zone.
(d) **Phytovolatilization:** converts a contaminant into a volatile form.
(e) **Rhizofiltration:** contaminants adsorbed to the roots (Susarla et al. 2002; Schwarzenbach et al. 2006; Van Aken 2008; Khalid et al. 2017).

5.4 Plant–Microbe Partnership for Improved Remediation of Pollutants

Plant and microbial partnership is a great approach for the removal of several groups of pollutants from the different environmental matrix. There are several reports present in the literature that showed the utility of plants for the removal of inorganic and organic pollutants from contaminated sites (Mishra et al. 2019; He et al. 2019; Navarro-Torre et al. 2017; Barac et al. 2004). Plants give shelter and food/nutrients to their adjacent rhizospheric and endophytic microbe. In exchange of that, the microbes support the plant growth by degrading and detoxifying the contaminants (Arslan et al. 2017; Vangronsveld et al. 2009; Shehzadi et al. 2014). Bacterial and PGPR associations interact with plants and can directly increase the remediation process by altering the metal availability through the production of phytohormones, phytochelors, change of pH, etc. Batty and Dolan (2013). In addition, bacteria associated with plants can degrade catabolic diversity, accumulate, and transform the organic compounds like PCBs, PAHs, pesticides, petroleum hydrocarbon, etc. (Hussain et al. 2018; Ibáñez et al. 2014; Abhilash et al. 2013; Männistö et al. 2001).

Dzantor (2007) reported that the microbial activity associated with plants can enhance the phytoremediation of organic xenobiotic compounds in the rhizosphere and stabilize them into less harmful metabolites. Heavy metals can be degraded up to a remarkable extent by plant-associated microbes such as rhizobacteria, mycorrhizae, and endophytic bacteria (Yousaf et al. 2014). The microbes have the capacity to modify the solubility and bioavailability of the heavy metals and also release some chelating substances that can change the redox potential of the soil. Abou-Shanab et al. (2003) reported that microbes like *Sphingomonas macrogoltabidus*, *Microbacterium liquefaciens*, and *M. arabinogalactanolyticum* reduce the soil pH to enhance the Ni uptake in *Alyssum murale* grown in serpentine soil. There are some other microbes like *Cellulosimicrobium cellulans,* a Cr-tolerant bacterium which has the ability to transform toxic Cr^{6+} to nontoxic Cr^{3+} form and also increased its uptake in the root and shoot parts of green chili (Chatterjee et al. 2009).

Similarly, *Bacillus* sp. and *Geobacillus* sp. isolated from As-contaminated soils have the capacity to biotransform toxic As^{3+} to its lesser toxic form As^{5+} (Majumder et al. 2013). The accumulation of heavy metals in the vacuoles of the plant is also reported such as vacuolar accumulation of Zn, Cu, and Cd was noticed in extraradical mycelium of *Rhizophagus irregularis* (Mishra et al. 2017) and Cd in *R. irregularis* in symbiosis with clover (Yao et al. 2014). It is evident that rhizospheric microbes have their own metabolic pathway that can degrade most of the organic pollutants. Chaudhry et al. (2005) reported that there is a significant decrease in the concentration of dichlorodiphenyldichloroethylene (DDE) in the rhizospheres of lucerne and ryegrass, zucchini, pumpkin, and spinach in the near-root zone as compared to that in bulk soil. Hsu and Bartha (1979) also noticed that organophosphorus insecticides like diazinon and parathion and herbicide 2,4-D not only got accumulated in the rhizosphere of bush bean (*Phaseolus vulgaris*) and sugar cane (*Saccharum officinarum*) but also degraded completely. A degradation study of 17α-ethynylestradiol (EE2) revealed that, when the microbe, *Hyphomicrobium* sp. combined with a hyperaccumulator plant like *Lolium perenne,* the remediation efficacy gets increased greatly (He et al. 2019).

Plant–microbe association has shown success in case of pharmaceuticals and personal care products (PPCPs) also, which have been categorized as emerging pollutants (Gerhardt et al. 2017); Liu and Wong 2013). For example, carbamazepine could be degraded with an endophytic bacteria isolated from *P. australis*. It has the capacity to degrade carbamazepine concentration by 35–66% from its initial concentration within 1–4 days (Sauvêtre and Schröder 2015). Many other endophytic microbes have also been reported to degrade carbamazepine, remarkably, like *Diaphorobacter nitroreducens*, *Achromobacter mucicolens*, *Chryseobacterium taeanense*, *Rhizobium daejeonense*, and *Pseudomonas moorei* (Nguyen et al. 2019). Another PPCP is ibuprofen (IBU) that can be degraded aerobically via species of family *Flavobacteriaceae, Methylococcaceae* etc. and anaerobically by family *Spirochaetaceae* and genus *Clostridium* (Li et al. 2013). Zhao et al. (2015) reported

90% degradation of Triclosan with three different wetland species, namely emergent *T. angustifolia*, submerged *Hydrilla verticillata*, and floating plant *Salvinia natans* in association with beta-, delta-, and gamma-Proteobacteria, Sphingobacteria, and Cyanobacteria. Several other examples of plant microbe association-mediated remediation are present in the literature, which are listed in Table 5.2.

Table 5.2 Plant-microbe interaction for remediation of pollutant

Pollutant	Microbes used	Plants used for phytoremediation	References
Cd	*Hyphomicrobium* sp. GHH	Ryegrass	He et al. (2019)
As, Cr, Cu, Ni, Pb, Zn	*V. kanaloae*, *Pseudoalteromonas*, *P. prydzensis*, *S. Warneri*, *K. marisflavi*, *M. aloeverae*, *B. vietnamensis*, *H. zincidurans*	*Arthrocnemum macrostachyum*	Navarro-Torre et al. (2017)
Chlorpyrifos	*Mesorhizobium* sp.	Ryegrass (*Lolium multiflorum*)	Jabeen et al. (2016)
Phenol	*Bacillus* spp.	*Vicia sativa*	Ibáñez et al. (2014)
Hexachloro-cyclo-hexane	*Sphingomonas herbicidovorans*	Maize (*Zea mays*)	Abhilash et al. (2013)
Trichloroethylene (TCE)	*Enterobacter* sp.	Poplar (*Populus trichocarpa*)	Kang et al. (2012)
VOCs and toluene	*Burkholderia cepacia*	Yellow lupine (*Lupinus luteus*)	Barac et al. (2004)
PCBs, Trichlorophenol (TCP)	*Herbaspirillum* sp.	Wheat (*Triticum aestivum*)	Männistö et al. (2001)
PCBs	*Pseudomonas fluorescens* sp.	Alfalfa (*Medicago sativa*)	Villacieros et al. (2005)
PCBs	*Pseudomonas putida*	*Arabidopsis*	Narasimhan et al. (2003)
Aroclor compounds (e.g., 1242, 1248, 1254, and 1260)	*Sinorhizobium meliloti*	Alfalfa (*Medicago sativa*)	Mehmannavaz et al. (2002)
Trichloroethylene (TCE) and Ni	*Burkholderia cepacia VM1468*	*Lupinus luteus*	Weyens et al. (2010)
Toluene	*Burkholderia cepacia*	*Zea mays* and *Triticum* sp.	Wang et al. (2010)
2,4,6-Trinitrotoluene	*Consortium*	*Agrostis* sp.	Thijs et al. (2014)
Pentachlorophenol (PCP)	*Sphingobium chlorophenolicum*	*Triticum aestivum*	Dams et al. (2007)
Bisphenol-A and (PCP)	*Coriolus versicolor*	Tobacco (*Nicotiana tabacum*)	Bhatia and Kumar (2011)

5.5 Transgenic Technology for Enhanced Phytoremediation

Although phytoremediation has been an efficient method for mitigation of water as well as soil pollution, the transfer of this technology from lab scale studies to field scale implementation is still a challenge. The introduction of transgenic plants in the field of environmental remediation has enhanced the practical applicability of plant-mediated treatment methods. The transfer of specific traits to transgenic plants not only alleviates the degradation of toxic/hazardous contaminants but also makes the process more time and cost efficient. The whole process of making a transgenic plant includes identification of specific catabolic genes responsible for carrying out degradation/mineralization, their isolation from plants/animals/microbes, and then transferring them to a suitable plant species (Aken et al. 2010).

Initially, transgenic plants were developed to reduce insect and pest damages and to increase crop yield in agriculture (Paul et al. 2017), but later on, they gained attention for environmental cleanup and were subsequently used in remediating contaminated soils (Kawahigashi (2009). The first report on transgenic plants was released in 1984 (Horsch et al. 1984). In 1986, France and the United States conducted the first field trials on tobacco, which was the first genetically engineered plant, aimed to induce resistance against herbicides in plant species. In 1992, China introduced a virus-resistant tobacco plant and became the first country to launch transgenic plant in commercial market. The first transgenic plant commercialized in Europe was a genetically modified tobacco plant which had tolerance against bromoxynil, an herbicide (Schütte et al. 2017). The European Union also gave its consent for its marketing, and subsequently, in 1995, the US Environment Protection Agency (EPA) too approved the Bt-Potato (Agnihotri and Seth 2019).

About 25% genera of the *Brassicaceae* family comprising of around 90 species have been identified as efficient hyperaccumulators for various heavy metals. *Brassicaceae* can accumulate selenium up to 100 times more if it is grown in seleniferous soils (Pilon-Smits and Quinn 2010). Brooks et al. (1998) mentioned that *Brassicaceae* family includes a large number of Ni-accumulating plants as well. Similarly, Nouairi et al. (2006) reported that *B. juncea* and *B. napus* can accumulate 1450 and 555 μg Cd/g dry wt., respectively. Species of genera like *Brassica, Arabidopsis, Alyssum,* and *Noccaea* are known to accumulate, remove, sequester, transform, and/or detoxify majority of heavy metals (Agnihotri and Seth 2019). The high capacity of plants belonging to *Brassicaceae* family towards metal accumulation indicate that the development of transgenic plants from *Brassicaceae* family having high rate of heavy metal accumulation such as *Noccaea caerulescens, Arabidopsis halleri*, and *Populus trichocarpa*, along with fast rate of growth and high biomass could be a solution for remediation of heavy metal contaminated soil in a much effective and time-efficient manner.

Apart from members of *Brassicaceae* family, there are other plant species also, which have been used successfully for the development of transgenic plants having improved phytoremediation potential. For instance, yeast cadmium factor (YCF1) protein which is known for its high tolerance towards Pb and Cd was transferred from yeast to *Arabidopsis thaliana* and was studied for the removal of Pb and Cd from contaminated soil (Bhuiyan et al. 2011). The results revealed that the YCF1 active plants have relatively high tolerance capacity against Pb and Cd, suggesting that these transgenic plants could be a potential tool for phytoremediation of other heavy metals also (Chen et al. (2013). It was further observed that the efficiency of YCF1 protein get enhanced up to 9 times when it was inserted into a vector named as YCF1-deletion mutant DTY167 (Bhuiyan et al. 2011). Transgenic *Arabidopsis* and tobacco plants were reported to overexpress the nicotinamine synthase gene, which is responsible for increased synthesis of nicotinamine in host plant.

The alleviated levels of nicotinamine subsequently enhances detoxification of metals particularly nickel (Kim et al. 2005). Another gene phytochelatin synthases gene (PCS) is known for regulating metal tolerance in plants. Zhang et al. (2018) isolated PCS (VsPCS1) from *Vicia sativa* for checking its role in regulating Cd tolerance in *Arabidopsis thaliana* and found a positive correlation between Cd tolerance and phytochelatin content in plants. Laccase (LAC) belonging to ceruloplasmin oxidase family regulates oxidation of monolignols to higher order lignins which are significant for plant development as well as metal tolerance. Liu et al. (2017) reported that OsLAC10 increases the process of root lignification in *Arabidopsis*, inhibiting excessive absorption of Cu, thereby improving the overall tolerance of the plant against Cu.

Transgenic plants have not shown success for heavy metal removal only, but organic contaminants have also been reported to degrade using transgenic methods. One of the genes, which has been reported to show tolerance against wide group of herbicides and pesticides, is cytochrome P450 monooxygenase (Zhang et al. 2015; Hussain et al. 2018). For instance, bispyribac sodium herbicide responsible for inhibiting the activity of acetolactate synthase could be detoxified using CYP72A31 present in indica variety of transgenic *Oryza Sativa* (Saika et al. 2014). Similarly, CYP72A31 present in transgenic *Arabidopsis* has also shown tolerance against bensulfuron methyl, an herbicide (Saika et al. 2014).

Genetically transformed tobacco plants having mammalian cytochrome P450 2E1 have been reported to degrade wide range of halogenated organic compounds like trichloroethylene, ethylene dibromide, carbon tetrachloride, chloroform, etc. (Doty et al. 2000). Singh et al. (2011) demonstrated enhanced tolerance of transgenic tobacco plants having CYP 2E1, against an organichlorine pesticide, Lindane in soil and hydroponic solution. Germaine and coworkers (2006) successfully degrade 2,4-dichlorophenoxyacetic acid (2,4-D) by the insertion of *Pseudomonas putida* (endophytic bacterium) strain VM1450 in to pea plant. Table 5.3 enlists different kinds of transgenes derived from source species and then inserted into target plant species to enhance phytoremediation capability of plant species. There are several other studies available in the literature which suggests that development of transgenic plants through recombinant DNA technology is a promising approach for improving the phytoremediation potential of plants.

Table 5.3 Different transgenes obtained from source species and inserted into a target plant to enhance phytoremediation potential

Source species	Target species	Transgenes used	Remarks	References
Thaliana	*N. tabacum*	Nicotianamine synthase (NAS1)	Increased Fe level in leaves of adult plants, enhanced accumulation of Zn and Mo, increased Ni tolerance	Douchkov et al. (2005)
E. coli	*B. juncea*		Accumulate more Se in their leaves.	Banuelos et al. (2007)
Arabidopsis	*N. tabacum*	Phytochelatin synthase (AtPCS1)	Cd^{2+} tolerance was increased, twofold increase in Cd^{2+} accumulation was observed in roots and shoots at seedling stage	Pomponi et al. (2006)
B. campestris	*A. thaliana*	Metallothioneins (MtTs) two MT genes, *BcMT1* and *BcMT2*	Improved Cd and Cu tolerance in transgenic plant	Lv et al. (2013)
A. thaliana	*N. tabacum*	AtMt2b	Increased transport of Cd and Zn to shoot	Grispen et al. (2011)
S. cerevisiae	*A. thaliana*	Protein YCF1, member of the ATP-binding cassette (ABC)	Enhanced tolerance towards Pb and Cd	Song et al. (2003)
Arabidopsis	*A. thaliana*	xcd2-D, codes for a zinc-finger transcription factor called as ZAT6	Increased Cd accumulation	Chen et al. (2016)
Bacillus megaterium	*A. thaliana*	Protein (MerP)	Higher tolerance and accumulation potential for Hg, Cd, and Pb	Hsieh et al. (2009)
Arabidopsis thaliana	*Oryza sativa*	AtPCS	Enhanced tolerance towards Cd stress	Venkataramaiah et al. (2011)
Cajanus cajan	*Arabidopsis thaliana*	Metallothioneins MT1	Better tolerance and accumulation against Cu and Cd	Sekhar et al. (2011)
Enterobacter cloacae	*B. napus*	ACC deaminase	Boosted tolerance and accumulation against As(V)	Nie et al. (2002)
Pseudomonas putida	*B. napus*	ACC deaminase	Enhanced tolerance and accumulation against Ni	Agnihotri and Seth (2019)

5.6 Nanotechnology to Enhance the Efficiency of Phyto-bio Remediation

Nanotechnology is a wide area focused on materials occurring on a very small scale. It deals with a structure which is having at least one dimension is in the range of nanoscale, i.e., 1–100 nm (Yadav et al. 2018). Nanoparticles (NPs) can be broadly divided into two parts: organic NPs; carbon NPs, i.e., fullerenes; inorganic NPs: magnetic NPs, metal NPs (Au, Ag), semiconductor (TiO_2, ZnO) (Lin and Xing 2007). Srivastava et al. (2018) reported that NPs are of three types: natural (e.g., volcanic or lunar dust, mineral composites), incidental (resulting from anthropogenic activity, e.g., diesel exhaust, coal combustion, welding fumes), and engineered (quantum dots, nanogold, nano zinc, nano aluminum, TiO_2, ZnO, and Al_2O_3). Nanoparticles exhibit a number of special properties such as high surface to-volume ratio, small enough to generate quantum effects, unique physicochemical properties, etc. and that is the reason nanoparticles are getting increasing interest in the field of science, engineering, cosmetics, pharmaceuticals, drug delivery, and also in environmental cleanup Das et al. (2015). In the area of environmental remediation, several types of nanoparticles such as metals (Zn, Fe, Ni, Pd, etc.), metal oxides (TiO_2, ZnO, Fe_2O_3, Fe_3O_4, MnO_2, etc.), and bimetallic (Pd/Fe, Fe/Ag, Cu/Ni, etc.) nanoparticles have been used successfully for the removal/degradation of wide array of inorganic and organic contaminants. The mechanism of nanoparticle-mediated remediation generally includes oxidation-reduction, ab/adsorption, precipitation, co-precipitation, catalytic degradation, etc. (Crane and Scott 2012; Singh and Misra 2016).

Basically cleanup process of contaminants is called as remediation. If a biological agent is involved in the removal of the pollutant/s, then it is called as bioremediation, whereas if it is done with the involvement of a plant species, then it will be referred as phytoremediation. The integration of nanotechnology with either of these methods has been proved as an effective alternative to the existing conventional methods of remediation. For instance, Jiamjitrpanich et al. (2013) combined nanotechnology and phytotechnology for remediation of trinitrotoluene (TNT) contaminated soil. When nanoscale zero-valent iron (nZVI) was added at different concentrations to the TNT-contaminated soil, the uptake of TNT by the roots of *Panicum maximum* was comparatively increased than those without nanoparticles. The removal efficiency was observed to be higher when the TNT-nZVI ratio was kept at 1:10. Another study also demonstrated that nZVI effectively improved the efficiency of different plant species like *Alpinia calcarata, Cymbopogan citratus*, and *Ocium sanctum* against the removal of an organochlorine pesticide, endosulphan (Pillai and Kottekottil 2016).

Similar kind of enhanced remedial efficiency has been reported in another study wherein Ag nanoparticles enhanced the accumulation of Pd, Ni, and Cd in maize inoculated with *Pseudomonas and Bacillus cereus*, respectively (Khan and Bano 2016). The increased efficiency of integrated method could be ascribed to nanoparticle-induced alleviated production of phytochromes [abscisic acid (ABA),

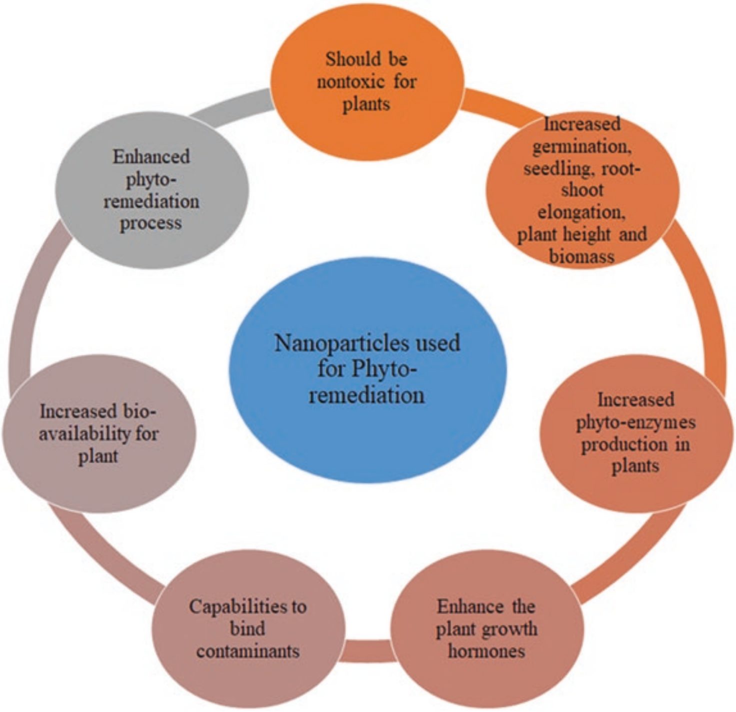

Fig. 5.3 Characteristics of nanoparticles suitable for phytoremediation

indole acetic acid (IAA), and Gibberellin (GA)] and proline in PGPR along with reduced oxidative stress. Salicylic acid nanoparticles were reported to enhance As tolerance in *Isatis cappadocica* (Souri et al. 2017). Similarly, nZVI showed positive effect on stabilization in sunflower rhizosphere (Vitkova et al. 2018). The major characteristics that should be present in nanoparticles to be used for enhancing phytoremediation potential of plant are presented in Fig. 5.3.

El-Kassas et al. (2016) biologically synthesized Fe_3O_4 NPs using two seaweeds, namely *Padina pavonica* (Linnaeus) *Thivy* and *Sargassum acinarium* (Linnaeus) and compared their Pb removal capacity. The findings revealed that Fe_3O_4 NPs entrapped alginate beads prepared from *P. pavonica* were smaller in size and have relatively higher Pb removal capacity (91%) than that of *S. acinarium* (78%). Liang et al. (2017) reported that nano-hydroxyapatite elevates Pb accumulation capacity (up to 46.55%) in Ryegrass plant species. In another phytoremediation study, the impact of different concentrations of nZVI (0, 100, 200, 500, 1000, 2000 mg/kg) on Pb accumulation capacity of Ryegrass species was studied for 45 days. Maximum Pb accumulation was noticed at nZVI concentration of 100 mg/kg. It was further noticed that lower nZVI concentration boosts Pd accumulation, but as the concentration goes up, the remedial efficacy of the plant gets reduced (Ding et al. (2017). The probable reason for decreased removal could be attributed to the critical oxidative stress caused by the higher concentration of nanoparticles in the plant (Huang et al. 2018).

The experimental study by Vasantharaj et al. (2019) is mainly focused on synthesizing eco-friendly and nontoxic metallic nanoparticles. The plant extracts of *R. tuberosa* was used to produce FeO NPs that were reported to be effectively used for bioremediation application. It showed potential antimicrobial activity against different Gram-positive and Gram-negative pathogens and also promoted successful degradation of synthetic dye like crystal violet. Table 5.4 enlists more examples of nano-phytoremediation below. Though nanotechnology has been evolved as a promising approach in the integrated phytoremediation study, the effect of nanoparticles on the non-target species is yet to be explored. There is a need for further research in this field to fully investigate the fate of nanoparticles in the environment.

5.7 Conclusions

Pollutants are ever increasing in the environmental ecosystem due to rapid industrialization, urbanization, non-mechanized agricultural practices, vehicular emissions, etc. In natural ecosystem, the speedy cleanup of the environment and stabilization of pollutant is extremely needed to support the sustainability of environmental ecosystems. Phytoremediation is a widely used remediation technique over the period of time, but the need of faster contaminant removal, consuming less time is a bit difficult to achieve with this technique leading further research in this domain. The presence of living plants and its association with native microbes in polluted region assist the phytoremediation technology making it more efficient in remediating organic and inorganic pollutants. Plant–microbial partnership could be further enhanced through genetic engineering which led the way for the development of transgenic plants. These plants are quite superior to the plants that naturally degrade the toxicants in terms of efficiency and time consumption. Besides, transgenic plants also facilitate the plant–microbe interaction and improve the microbial activities at rhizosphere for increased pollutant uptake and their removal from environmental systems. Though transgenic plant systems are much hyped removal technology to the date, the biochemical activities and transport mechanism inside the plant are still not fully explored and need further research to make them more pollutant selective and transferring it to target cell type without interfering in other cell functions. Integrated nano-phytoremediation technology also holds great promises towards environmental cleanup; however, uncertain fate of nanoparticles in the environment and toxicity towards non-targeted species is not fully understood and yet to be explored further.

Table 5.4 List of species and nanomaterials used for contaminant removal

Species	Nanomaterials	Contaminants	Remarks	References
Alpinia calcarata, Ocimum sanctum, Cymbopogon citratus	nZVIs	Endosulfan	Removal efficiency is ≈100 (%), 76.28 (%), 86.16 (%) respectively	Srivastava et al. (2018)
Panicum (*Panicum maximum Jacq*.)	nZVI	Trinitrotoluene (TNT)	The removal efficiency of TNT increased from 85.7 to 100% after 120 days	Jiamjitrpanich et al. (2013)
Maize (*Zea mays L*.)	Silver nanoparticles	Cd, Pb, and Ni	Enhanced accumulation of Cd, Pb, and Ni in shoot	Khan and Bano (2016)
Ryegrass (*Lolium perenne L*.)	Nano hydroxyapatite	Pb	Removal efficiency was increased from 11.67 to 21.97% under Pb stress of 800 mg/kg	Jin et al. (2016)
Sunflower (*Helianthus annuus L*.) and ryegrass (*Lolium perenne L*.)	nZVI	As, Cd, Pb, and Zn	The concentrations of As, Cd, Pb, and Zn in roots and shoots decreased by 50–60% as compared to the control sample	Vitkova et al. (2018)
Collard greens (*Brassica oleracea L*.)	Multiwall carbon nanotubes	Carbamazepine	The functionalization of carbon nanotubes enhanced carbamazepine translocation	Jin et al. (2016)
Zucchini (*Cucurbita pepo L*.) and soya bean [*Glycine max (L.) Merr*.]	Ag nanoparticles	p,p'-DDE	Decreased the uptake and accumulation of p,p'-DDE in both the plants	Jiamjitrpanich et al. (2013)
Ramied seed (*Boehmeria nivea*)	Starch stabilized nZVI	Cd	Increase Cd-accumulation in roots, stems and leaves by 16–50%, 29–52%, 31–73% respectively in Ramied seed	Gong et al. (2017)
Soya bean plant (*Glycine max*)	TiO_2 NPs	Cd	Accumulation of Cd in the roots, stems, and leaves of soya bean increased by 2.5, 2.6, and 3.3 times, respectively	Singh and Lee (2016)
Eastern cottonwood (*Populus deltoids*)	Fullerene NPs	Trichloroethylene	Uptake increased from 26 to 82%	Ma and Wang et al. (2010)

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Chapter 6
Bioprocessing of Cane Molasses to Produce Ethanol and Its Derived Products from South Indian Distillery

**Sankaran Krishnamoorthy, Premalatha Manickam,
and Vijayasekaran Muthukaruppan**

Abstract Ethanol is a primary renewable fuel and it has become a basic chemical for the production of various valuable products. It poses the same chemical properties regardless of the feedstocks from which it is produced. The production of ethanol is largely carried out by fermenting the sugars and starch in distilleries. This technique is considered as a matured technology which includes the steps like feed preparation, fermentation, distillation, and dehydration. This chapter deals with the industrial scale practice of producing ethanol and its derived product in southern Indian distilleries. It also explains the practical treatment of wastewater generated out from the ethanol industry. As the ethanol market is steadily increasing, there are potential opportunities to increase the production efficiency of ethanol and to reduce the associated cost besides increasing the number. The boom in ethanol production has believed to be a driver of economic development by adding substantial value to agricultural commodities.

Keywords Ethanol · Fermentation · Distillation · Dehydration · Wastewater treatment

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6.1 Ethanol

Ethanol or ethyl alcohol (formula: C_2H_5OH) is a clear, colorless liquid with a characteristic sweet flavor in dilute aqueous solution and it gives a burning taste in more concentrated forms (https://www.calstatela.edu/sites/default/files/dept/chem/07summer/158/25-words ethanol.pdf 2018). Ethanol is the intoxicating component in the alcoholic beverages such as beer, wine, and others. It is also been used as a biofuel in many countries across the world. Ethanol molecule contains carbon, hydrogen, and oxygen atoms in its structure (Fig. 6.1).

Single lines between the atoms denote single covalent bond. Each carbon atom has four bonds; oxygen atom has two bonds; hydrogen atom has one bond. In the initial days, ethanol is produced from ethene (obtained from fractionation of crude oil) with steam. Phosphoric acid is used as a catalyst in this reaction which is written as follows,

$$C_2H_4 + H_2O \overset{H_3PO_4}{\rightarrow} C_2H_5OH \tag{6.1}$$

In this process, ethanol is the only product and ethene and steam are the reactant. Though it is an efficient process, ethene is fractionated from crude oil and thus, it is a non-renewable source. The depletion of non-renewable source is a major threat for this process and so there is a need to search for alternatives (http://www.bbc.co.uk/schools/gcsebitesize/science/aqa/substancesfromcrudeoil/polymersandethanolrev4.shtml 2018).

Yeast is found to be a natural catalyst which can convert sugar from plant material to ethanol and carbon dioxide by the process of fermentation. The fermentation reaction is given below:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \tag{6.2}$$

Unlike the chemical process, the process does not require reaction at higher temperature and it occurs in ambient temperature. Further, the sugar from plant material is a renewable one (http://www.bbc.co.uk/schools/gcsebitesize/science/aqa/substancesfromcrudeoil/polymersandethanolrev4.shtml 2018). Ethanol can be produced from many kinds of plant materials that contain sugar, starch, or cellulose

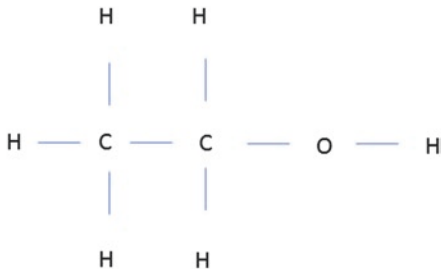

Fig. 6.1 Structural formula of ethanol

(Naik et al. 2010). Plant materials can be categorized into three groups from which ethanol can be produced:

1. sugar materials such as sugarcane, beet, sweet sorghum, and fruits;
2. starchy materials such as wheat, corn, rice, potato, cassava, sweet potatoes; and
3. cellulose materials such as wood used paper, agricultural crop residues.

Ethanol produced from the first and second group of plant materials are referred as first generation ethanol. The third groups of cellulosic materials are obtained in the form of biomass. The ethanol production from the biomass or the waste is now considered with high importance.

6.2 Ethanol in India

Ethanol production in distilleries depends on the local source of plant material and its growth on the prevailing environmental conditions and sustainability. The distilleries use molasses, cereals, and other agricultural products for the production of alcoholic beverages. Molasses based distilleries are prevalent in India. Molasses are obtained from sugar industries and have the source either from sugarcane or beet sugar. Many industries in India utilize sugarcane molasses for the production of ethanol.

A large number of sugar industries are established in the country since 1932 and the major industries are located in the state of Maharashtra and Uttar Pradesh. Both the states are having good irrigation facilities for the cultivation of sugarcane. During recent years, India has become the largest producer of sugarcane in the world. This resulted in the large availability of cane molasses to produce ethanol. Thus, distilleries are encouraged to utilize the molasses for the production of ethanol. Distilleries are more in the state of Maharashtra, Uttar Pradesh, Andhra Pradesh, Madhya Pradesh, Tamil Nadu, and Karnataka (Shrivastava et al. 2011).

There are 325 distilleries in India that approximately produce 2.7 billion liters of ethanol and 40 billion liters of wastewater yearly. Of the total output of ethanol, 50–52% is utilized by the industry for the production of derived products such as acetaldehyde, acetic acid, and ethyl acetate. The rest of ethanol is used for potable purposes for the preparation of wine, whisky, and brandy (Sankaran et al. 2014). The application of ethanol now becomes widespread and it acts as a basic material for rapidly developing chemical and bio industry. Further, ethanol is an important available source of energy. Therefore, in the present scenario, the demand for the ethanol will increase rapidly and it forces the increase of a number of distilleries in India. As the production increases, the wastewater generation will also increase which needs proper treatment before disposal.

6.3 Ethanol Production in South Indian Distilleries

In industrial scale, ethanol is produced by the fermentation of sugarcane molasses. Molasses are said to be the mother liquor left after the crystallization of sugarcane juices. It is a dark brown color viscous liquid which contains around 60% of fermentable sugars. The flow diagram (Fig. 6.2) illustrates the ethanol production process in a southern Indian distillery (M/s Trichy Distilleries and Chemicals Ltd.)

6.3.1 Feed Preparation

The first step in the ethanol production is to prepare the feedstock. Cereal grains such as corn, rice, barley, soybean, wheat, and molasses are the major sources of the feedstock. Molasses is diluted with water in the ratio of 1:5 (v/v) and the nitrogen content is checked. If it is less, then the molasses is fortified with diammonium phosphate or urea to provide adequate nitrogen supply to yeast cells. Then the pH is further adjusted by adding sulfuric acid which favors the growth of yeast and minimizes the growth of contaminating bacteria. The molasses solution is clarified and heated to a high temperature for 20–30 min to avoid bacterial contamination.

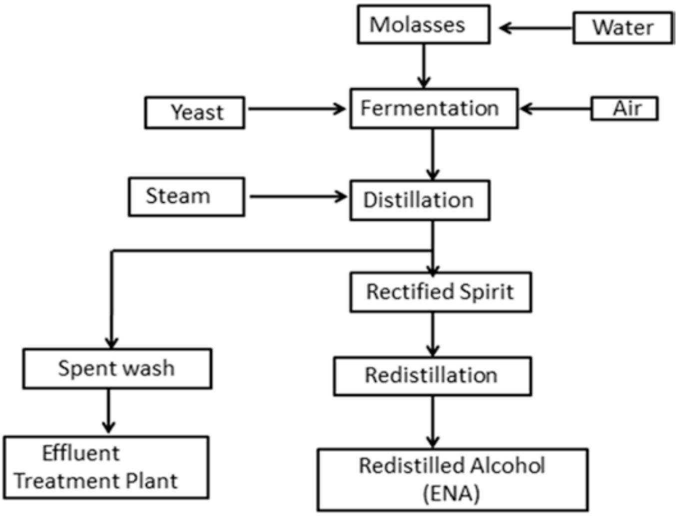

Fig. 6.2 Flow diagram of ethanol production in a distillery

6.3.2 Fermentation of Sugars by Yeast: Ethanol Production

The contamination free molasses solution is added with activated yeast in a larger reactor at 30 °C. The fermentation is carried out for 2–3 days in a closed reactor. Molasses have 50–55% concentration of sucrose with the chemical formula $C_{12}H_{22}O_{11}$. Enzymes from the yeast cells (*Saccharomyces cerevisiae*) such as invertase and zymase act on the molasses and convert it into ethanol in two steps as per the reaction is given below:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6 \tag{6.3}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2 \tag{6.4}$$

The fermentation process also has a side reaction given below

$$2C_6H_{12}O_6 + H_2O \rightarrow ROH + RCHO\left(\text{high molecular weight alcohols}\right) \tag{6.5}$$

The process of fermentation can be carried out in (1) batch mode and (2) continuous mode. Figure 6.3a, b illustrates the fermentation process of ethanol production.

Other chemicals used in the fermentation process are listed below:

- Sodium metabisulfite (SMBS): antibiotic for the fermentation process
- Caustic soda NaOH: cleaning purpose
- Boiler chemicals: oxygen scavenger, anti-scaling agent
- Sodium chloride (NaCl): softener regeneration

It is important to note that the impure culture of yeast may produce varying amounts of other substances which include glycerin, methanol, and various organic acids. After fermentation process, the fermented liquid is subjected to the process of distillation to separate ethanol from the fermented liquid.

6.3.3 Distillation Process

6.3.3.1 Rectified Spirit

Ethanol obtained from the fermentation is called as “fermented wash” which has the purity only up to 14%. The balance portion majorly contains water and other fermented compounds. Distillation helps to separate ethanol from other components. The boiling point of ethanol is 78.4 °C which is lower than the boiling point of pure water (100 °C).

Modern distillation systems are multistage, continuous, countercurrent, vapor-liquid contacting systems that operate within the physical laws which state that

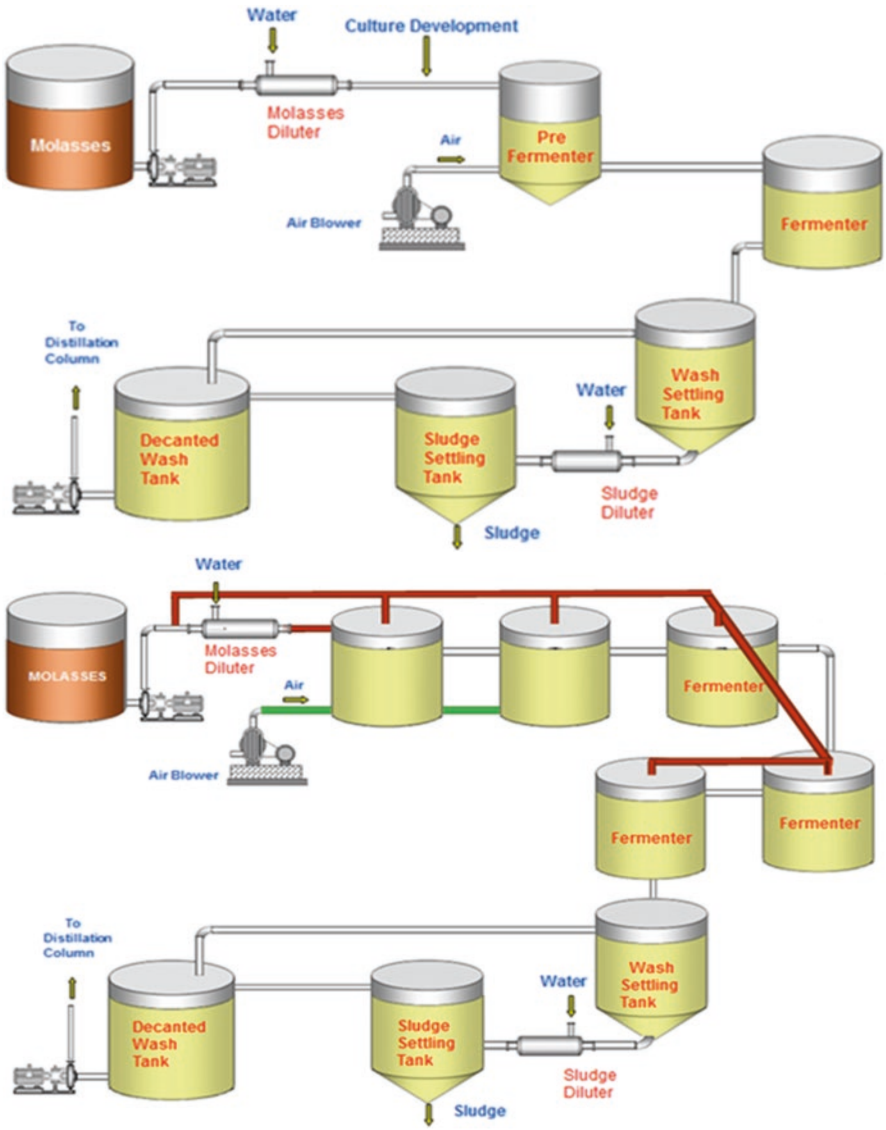

Fig. 6.3 (**a**) Batch fermentation. (**b**) Continuous fermentation. (Source: M/s Trichy Distilleries and Chemicals Ltd. (TDCL), Tiruchirappalli, India)

different materials boil at different temperatures (Fig. 6.4). A feed composed of two components which are to be separated. An energy source is required for driving the process (in the majority of the cases, this energy source is a steam which can enter either directly from the base of the tower or transferring its energy to the tower contents through a reboiler). An overhead purified product consisting primarily of the feed component with the lower boiling point, a bottom product containing the

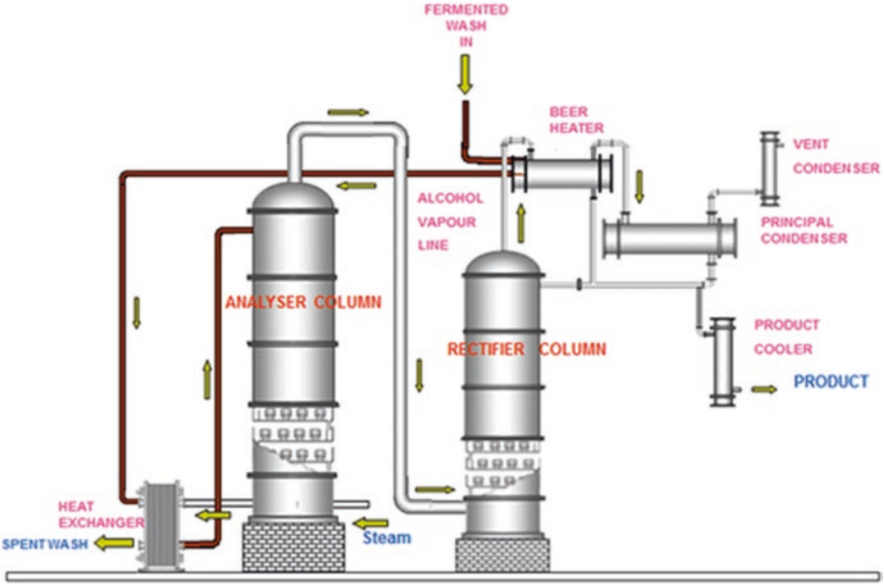

Fig. 6.4 Distillation process and separation of rectified spirit. (Source: M/s Trichy Distilleries and Chemicals Ltd. (TDCL))

component of the feed possessing the higher boiling point, an overhead heat exchanger (condenser), normally water cooled, to condense the vapor resulting from the boiling created by the energy input.

The overhead after condensation is split into two streams. One stream is the product from overhead and the other one is the reflux that is returned to the top of the tower for supplying the downflow liquid required in the upper portion of the tower. The distillation operation leads to obtaining the ethanol up to the concentration of 95–96% since the boiling point is not differing largely and it forms an azeotropic mixture with water. Ethanol of this purity is generally referred as “*Rectified spirit”* or “*Rectified Alcohol*.”

The ISI (Indian Standards Institution) specification of rectified spirit is given in Table 6.1.

6.3.3.2 Neutral Spirit or Neutral Alcohol

Rectified spirit is not completely neutral as it has a lot of impurities. Rectified spirit is redistilled to produce neutral alcohol or extra neutral alcohol (ENA). Figure 6.5 shows the production of ENA at *M/s* Trichy Distilleries and Chemicals Ltd.

The ISI specification for neutral spirit is given in Table 6.2.

Table 6.1 The ISI (Indian Standards Institution) specification of rectified spirit

S. no.	Characteristics	Requirement
1	Appearance	Clear, colorless
2	Ethyl alcohol content in degrees over proof	66.0° OP (min)
3	Specific gravity at 60 °F	0.8171 (max)
4	Miscibility with water (1:19) by volume	Miscible
5	Alkalinity	Nil
6	Acidity, percent by weight as acetic acid	0.002 (max)
7	Residue on evaporation percent by weight	0.005 (max)
8	Aldehydes content gram per 100 mL	0.006 (max)
9	Methyl alcohol content	Passes the test
10	Fuel oil	Passes the test
11	Furfural content	Passes the test
12	Ester content g per 100 mL of ethyl acetate	0.020 (max)
13	Copper content g per 100 mL	0.0004 (max)
14	Lead content g per 100 mL	0.001 (max)

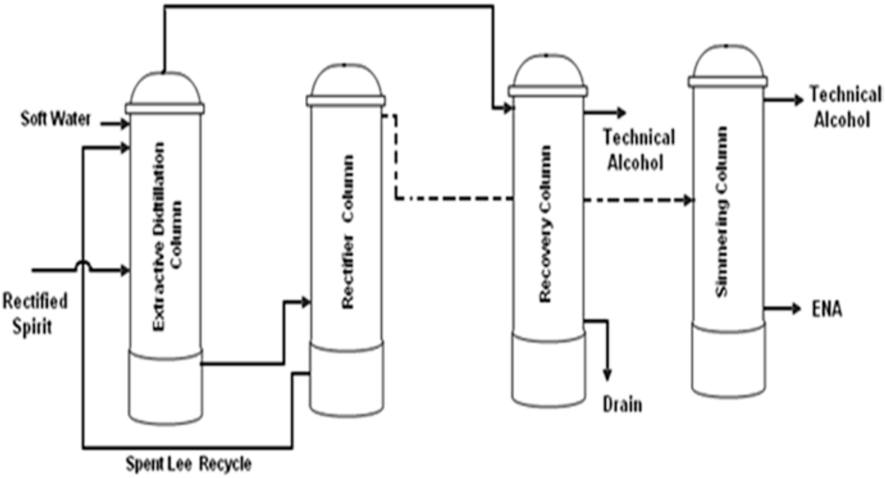

Fig. 6.5 Distillation process: extra neutral alcohol

6.3.4 Dehydration of Ethanol

Ethanol in pure form is not obtained from distillation since it forms an azeotrope with water (96% v/v). Absolute ethanol can be produced by dehydration of rectified spirit. Major Indian industries follow two methods to dehydrate the rectified spirit:

Table 6.2 The ISI specification for neutral spirit

S. no.	Characteristics	Requirement
1	Relative density at 15 °C	0.81245–0.81679
2	Ethyl alcohol content % by volume at 15.6 °C	94–96
3	Miscibility with water	Miscible
4	Alkalinity	Nil
5	Acidity (as CH_3COOH) g/100 mL	0.002 (max)
6	Residue on evaporation g/100 mL	0.002 (max)
7	Esters (as $CH_3COOC_2H_5$) g/100 mL	0.002 (max)
8	Lead (as pb) g/100 mL	Nil
9	Methyl alcohol content	Passes the test
10	Furfural content	Passes the test
11	Permanganate reaction time	30 min (max)
12	Aldehydes (as CH_3CHO) g/100 mL	0.004 (max)
13	Copper (as cu) g/100 mL	0.0002 (max)
14	Isopropyl alcohol acetone and other ketones	Passes the test

- Azeotropic distillation
- Molecular sieve technology

6.3.4.1 Azeotropic Distillation

This technology applies the use of a third substance called“entrainer” such as trichloroethylene, benzene, toluene, cyclohexane, and other to dehydrate the azeotropic mixture of ethanol with water. The entrainer alters the relative volatility of water and breaks the azeotropic point of ethanol and water. For instance, the ethanol–water system forms a minimum-boiling azeotropic mixture at 89.4 mole% ethanol at 78.15 °C. Benzene (80.2 °C) addition acts as the entrainer that forms a new minimum-boiling azeotrope with 23.3 mole % water, 22.8 mole % ethanol, and 53.9 mole % benzene. This mixture boils at 64.86 °C leaving as the product obtained from the overhead of the first column. Relatively pure ethanol leaves the column as a bottom product.

6.3.4.2 Molecular Sieve Technology

The molecular sieve technology uses the phenomenon of adsorption to dehydrate the azeotropic mixture of ethanol with water. It has become the best attractive option for industries due to less energy requirement compared to azeotropic distillation, less operational cost, and the technology is free from added chemicals. The industrial process of dehydrating ethanol using molecular sieve technology essentially involved introducing the azeotropic ethanol through a column of molecular sieve (zeolite balls) which adsorbs the water molecules on its surface from the mixture while passing the ethanol molecules. The dehydration unit operates with two adsorbers with the alternate steps of adsorption and desorption. Adsorption occurs in the vapor phase and under pressure. Desorption regenerates the water saturated molecular sieves. This step is performed under vacuum. Thus the drying out of ethanol is taking place.

6.4 Derived Products from Ethanol

6.4.1 Acetaldehyde

Acetaldehyde is produced by oxidation with air in the gas phase using a silver catalyst. The reaction is highly exothermic. The reaction mixture contains mainly unconverted ethanol and the acetaldehyde which is absorbed in an ethanol–water mixture and distilled to give acetaldehyde. Ethanol is recovered from the bottom stream and it is recycled to the process (https://chematur.se/process-areas/bio-chemicals 2018). The reaction is given below:

$$C_2H_5OH + \frac{1}{2}O_2 \rightarrow CH_3CHO + H_2O \tag{6.6}$$

The flow diagram explains the industrial process of acetaldehyde production from ethanol (Fig. 6.6).

6.4.2 Acetic Acid

Acetic acid is obtained by oxidizing acetaldehyde with air in the liquid phase using a dissolved catalyst (magnus acetate/potassium permanganate). The product from the reaction contains acetic acid, unreacted acetaldehyde, and peracetic acid which is further heated and passed through an another reactor in which the peracetic acid is reduced to acetic acid. Acetaldehyde is stripped away and it is recycled to the process. In a final distillation, the water is removed leaving glacial acetic acid (99.5%) as the bottom product which is further cooled and sent to storage (https://chematur.se/process-areas/bio-chemicals 2018). The reaction is given below:

$$CH_3CHO + \frac{1}{2}O_2 \rightarrow CH_3COOH \tag{6.7}$$

The flow diagram for the process is given in Fig. 6.7.

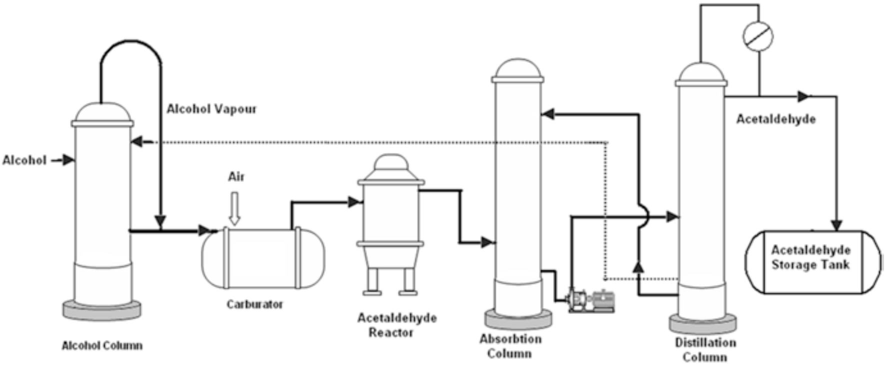

Fig. 6.6 Acetaldehyde production from ethanol

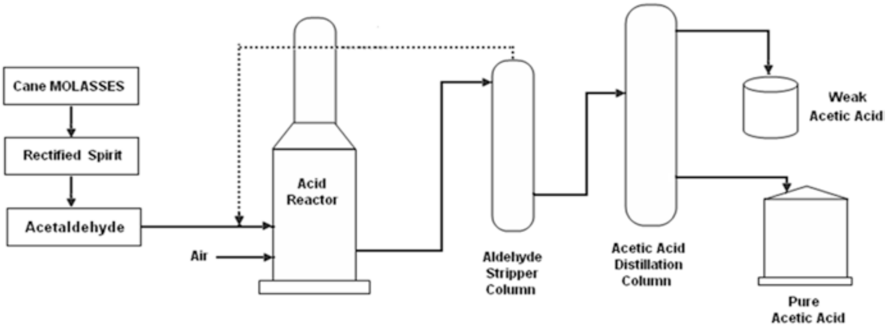

Fig. 6.7 Acetic acid production from acetaldehyde

6.4.3 *Ethyl Acetate*

Ethyl acetate is produced by esterification of acetic acid with ethanol using sulfuric acid as a catalyst. Ethanol and acetic acid are continuously fed to a reactor heated with steam. The ethyl acetate so formed is removed from the top of the reactor column together with some ethanol and water. The oily phase is further separated and washed and then sent to the ester column where the product is removed from the bottom. Water phases from decanters are sent to the recovery column in which ethanol is recovered and sent back to the reactor. The bottom water phase is sent out as a wastewater (https://chematur.se/process-areas/bio-chemicals 2018). The reaction is given below:

$$C_2H_5OH + CH_3COOH \rightarrow CH_3COOC_2H_5 + H_2O \qquad (6.8)$$

The flow diagram for the process is given in Fig. 6.8.

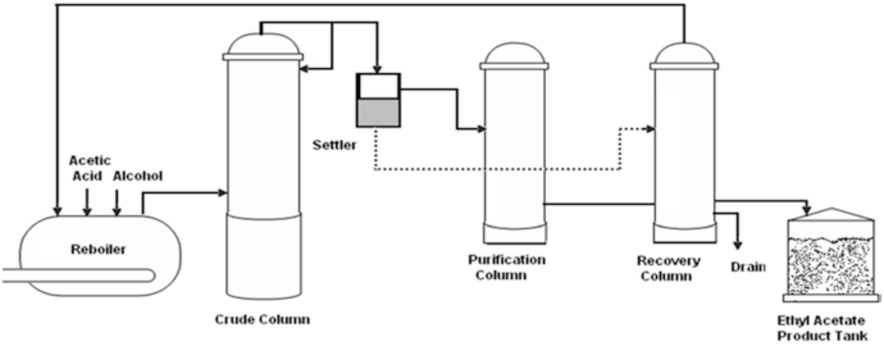

Fig. 6.8 Ethyl acetate production from ethanol and acetic acid

6.5 Uses of Ethanol

Besides ethanol proportion in alcoholic beverages listed in Table 6.3, it is largely used in personal care and pharmaceutical industries.

Personal care products such as hairspray, mouth wash, many deodorants, hand sanitizers, shampoos, soaps, perfumes, and aftershave lotions use ethanol in large amounts. Ethanol is used as a prime carrier for whole spectrum of medicine that includes cough, decongestants, and iodine solution. In addition, it is used as a solvent in processing vaccines, antibiotics, vitamins, and tablet. Household disinfectant spray and other cleaning agents use maximum proportion of ethanol. Ethanol is widely used as an available fuel. It is most often used as a motor fuel, mainly as a biofuel additive to gasoline. Ethanol has a gasoline gallon equivalency of 1.5 (1 volume of gasoline is equal to 1.5 times volume of ethanol in terms of energy).

Fiat 147 is the first car run entirely on ethanol and was introduced in the market in the year 1978 by Fiat in Brazil. In the USA, most cars on the road can run on fuel blended with 10% ethanol. Nowadays, many flexible vehicles are coming to the market which will run entirely on ethanol. The application of ethanol keeps increasing day by day. So, the production of ethanol is expected to increase in near future and thus the generation of wastewater also increases. Distillery adopts series of treatment steps to achieve zero liquid discharge (ZLD) as instructed by Central Pollution Control Board (CPCB).

6.6 Wastewater Generation from Ethanol Production and Its Treatment Practices

There are two types of wastewater generated in ethanol producing industry (Distillery). One is the non-processed wastewater which is relatively pure and it can be recycled. Another one is the processed wastewater that consists of fermented

Table 6.3 Ethanol proportion in alcoholic beverages

S. no.	Beverages	Alcohol by volume (ABV) range (%)
1	Beers	3–15
2	Wines	8–17
3	Fortified wines	15–22
4	Spirits	30–40
5	Fruit juices	<0.1
6	Cider, wine coolers	4–8

Table 6.4 Spent wash characteristics from a distillery—Analyzed as per APHA Protocol, 21st Edition, 2005

Parameters	Concentration range
Color	Dark brown
Odor	Sugar smell
Temperature	80–90 °C
pH	4–4.6
Conductivity	26–31 mS/cm
Inorganic TDS	17,160–20,460 ppm
TDS	85,000–1,10,000 ppm
TSS	4500–7000 ppm
COD	85,000–1,10,000 ppm
Acidity	5200–8000 ppm
BOD	25,000–35,000 ppm
Sulfate	13,100–13,800 ppm
Ammoniacal nitrogen	800–1100 ppm
Chlorides	4500–8400 ppm
Phenols	3000–4000 ppm
Phosphate	1500–2200 ppm
Total nitrogen	4200–4800 ppm

Note: *°C* degree celsius, *mS/cm* millisiemens/centimeter, *ppm* parts per million

sludge, spent less, and spent wash. Fermented sludge majorly contains yeast cell which can be recycled to the fermentation unit after dilution. Spent less is released from the rectified column of distillation unit may be cooled and recycled. The spent wash is largely released from the distillery and it counts approximately 15 KL for the production of 1 KL of ethanol.

The reason for the higher pollution load in the spent wash is due to the presence of organic compounds such as polysaccharides, reduced sugars, lignin, melanoidin, waxes, and inorganic compounds such as potassium, chlorides, sulfates, and phosphates (Bharagava and Chandra 2010; Sankaran et al. 2014). The characteristics of spent wash are given in Table 6.4.

Many technologies are providing the promising treatment strategy for the distillery wastewater. However, it is not taken to industrial scale so far. Distilleries at the southern region of India achieve ZLD mainly through anaerobic digestion, reverse osmosis (RO) plant followed by biocomposting since it possesses various advantages that include the generation of biogas, recovery of clean water, and biocompost, respectively (Sankaran et al. 2017). Figure 6.9 illustrates the stages of wastewater treatment in a distillery.

6.6.1 *Anaerobic Digestion*

It is a very conventional technique and still holds good in tackling the spent wash (wastewater) generated after ethanol separation. Anaerobic digestion effectively removes up to 90% of chemical oxygen demand (COD), 80–90% of biological or biochemical oxygen demand (BOD) along with the biogas generation up to 85–90%. The generated biogas can further be used to generate electricity and helping the distillery to meet out power requirement (Pant and Adholeya 2007). The anaerobic digestion process is mediated by methanogenic bacteria and the process of digestion is given in Fig. 6.10. Various configurations of anaerobic digesters are in use to serve the purpose in a more efficient way (Satyawali and Balakrishnan 2008).

6.6.2 *Reverse Osmosis*

Reverse osmosis is a separation process where dissolved inorganic substances such as salts are removed from a solution such as water. The RO Plant consists of the filter pump, prefilters (sand and cartridge filter), high-pressure pump, DT-modules (membranes), servo motor control valve, controls, and externally fitted degasser.

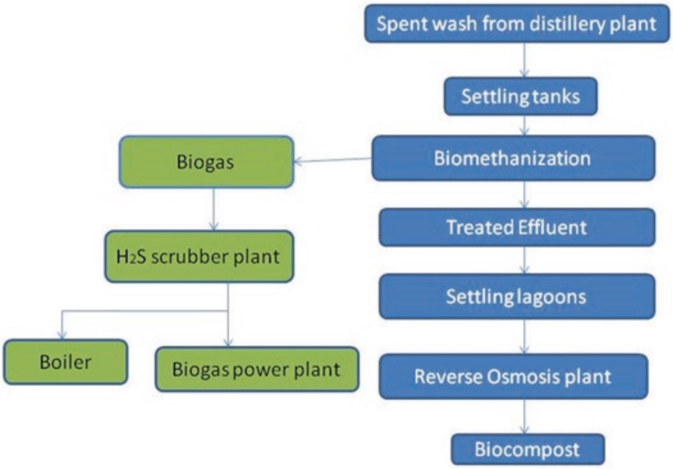

Fig. 6.9 Wastewater treatment stages of a distillery wastewater treatment plant

The components are mounted on skid frames. The units are programmed and controlled by a control unit which is fitted inside the control cabinet. The treated wastewater from the anaerobic digestion is passed to the RO plant. As a result, the pure water (permeate) is removed from the wastewater and recycled back to the fermentation unit. The concentrated wastewater (reject) is further sent for biocomposting.

6.6.3 Biocomposting

Scientific composting can overcome the problem of disposal of spent wash. It converts the organic waste into valuable resources. The spent wash is mixed with press mud (other waste received from sugar industry) for biocomposting. The process detail is highlighted below:

- Spent wash to press mud ratio is 2.5: 1 for 45 days cycle.
- Then windrows are prepared with press mud on biocompost yard.
- Sufficient space is given for aerotiller movement in between two windrows.
- Fresh press mud has 70–80% moisture, and it is reduced up to 50% by drying. Then increase the moisture up to 70% by spraying the distillery wastewater (spent wash).
- Thereafter, inoculum is added (1 kg inoculums/metric tonne of press mud) and properly mixed with the help of aerotiller. When the temperature gets increased it indicates that the microorganisms' activation has started.
- During the process, 50% moisture is maintained with the help of spent wash spraying. When the temperature gets decreased it indicates that the biocomposting

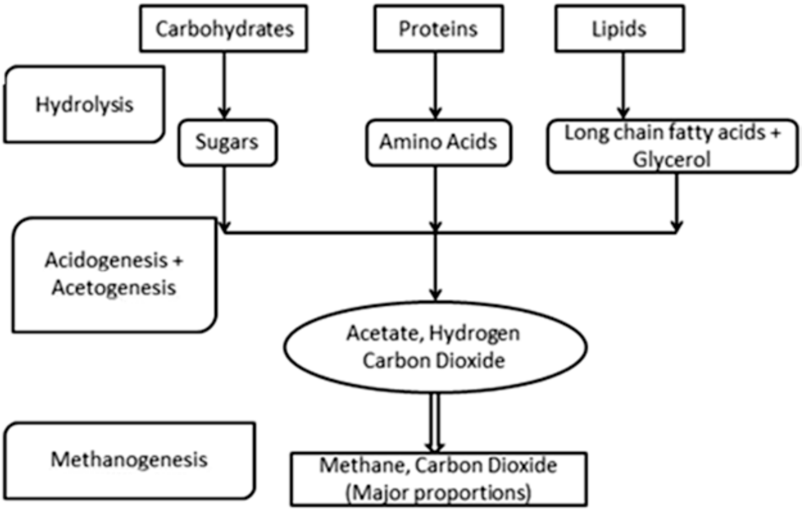

Fig. 6.10 The process of anaerobic digestion used for the treatment of distillery wastewater

process is completed. Then stop the spent wash spraying and reduce the moisture up to 30% in compost by drying.
- The biocompost also helps to improve the soil fertility.

Factors affecting the composting process include: (a) oxygen and aeration; (b) nutrients (C: N ratio); (c) moisture; (d) porosity, structure, texture, and particle size; (e) temperature; and (f) time duration.

6.7 Concluding Remarks

The demand for ethanol is steadily improving which in turn reflects the distillery not only to increase the number but also look for the new feed stocks and continuous improvement in the microbiological processes which include genetic manipulation of yeast cell and utilization of other microorganisms for ethanol production. The process of ethanol generation has been considered a mature technology. However, there are opportunities to take up the research in the area of reduction of sugar losses, avoidance of bacterial contamination, engineering yeast cells, development of fermentation process for alternative feed stocks, reduction of wastewater volume, novel techniques to generate energy from the wastewater and the recovery of valuable products from the wastewater. This movement of technology will improve the efficiency of process and the cost reduction. Thus, the fusion of research and transfer of technology to distillery will ensure the sustainable production of ethanol in the near future.

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Chapter 7
Biological and Nonbiological Approaches for Treatment of Cr(VI) in Tannery Effluent

Asma Kalsoom and Rida Batool

Abstract Leather tanneries are major source of hexavalent chromium contamination in the biosphere. Chromium (Cr) is being considered as an essential heavy metal extensively used in different industrial sectors for example, leather, paint, textile, and electroplating. A characteristic feature of chromate is its environmental mobility and consequently is a cause of environmental risk. Cr(VI) belongs to group A human carcinogen due to its mutagenicity, carcinogenicity, and teratogenicity in plants, animals, and humans, therefore causing serious health issues in all living beings. Conventional methods for chromate removal includes ion exchange, chemical precipitation, reverse osmosis, and electrochemical from tannery effluents. These procedures are effective but require high energy and chemical consumption that may produce secondary problems such as corrosion, spillage, and toxicity. So, the need of the hour is to develop eco-friendly techniques for efficient Cr(VI) removal. Therefore, bioremediation is an effective alternate for reclamation of contaminated sites. Bioremediation is the biological approach to degrade heavy metals using indigenous microorganisms. Microbes such as bacteria, fungi, yeast, and algae have the ability to survive under harsh environmental conditions. These microbes are proficient to reduce toxic Cr(VI) into less toxic Cr(III) by various cellular mechanisms. Therefore, environment friendly, economical, and effective strategies are needed to reduce chromate pollution in the surroundings. Thus, this chapter gives detailed information on production and properties of tannery effluent, environmental pollution, and health hazards of tannery effluent, biological and nonbiological methodologies for the effluent remediation. Moreover, the pros and cons of current processes have also been briefly discussed in this chapter.

Keywords Tannery effluent · Hexavalent chromium · Environmental and health issues · Bioremediation · Conventional methods

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7.1 Introduction

Chromium (Cr) is a heavy metal naturally present in two oxidation states i.e., Cr(III) and Cr(VI). Cr is generally dispersed in fresh water, rocks, and oceans (Krishnamurthy and Wilkens 1994; Saxena et al. 2019; Mishra and Bharagava 2016). Nutritionally, trivalent chromium is an essential part of balanced diet for humans and animals that maintains and inhibits adverse effect on metabolic processes of fats, carbohydrates, and protein synthesis (such as raised fasting insulin, reduced glucose tolerance, high cholesterol and triglycerides, and hypoglycemic symptoms) (Raman et al. 2018; Anderson 1989, 1997). Cr is also used for production of cement, stainless steel, paint pigments, wood preservatives, leather, etc. The dissemination and concentration of Cr in different environmental samples is summarized in Table 7.1. For freshwater life, the recommended guidelines are 8 μg/L for Cr(III) and 1 μg/L for Cr(VI), for marine life 50 μg/L for Cr(III) and 1 μg/L for Cr(VI), for irrigation water 5 μg/L for Cr(III) and 8 μg/L for Cr(VI), and for drinking water is 50 μg/L for Cr(VI) (Krishnamurthy and Wilkens 1994; Pawlisz 1997).

For the past few years, anthropogenic activities have contributed to ecological contamination, causing an increase in concentration of various heavy metals for example, chromium, selenium, lead, cadmium, mercury, etc. Industrial waste is disposed of in the nearby water bodies and ultimately absorbed in the surroundings. These heavy metals are utilized in several industries such as tanneries, electroplating, mining, textiles, pesticide industries, etc. (Vendruscolo et al. 2017; Kishor et al. 2019). Environmental pollution has affected various illnesses as they have crossed the recommended threshold limit value given by WHO (World Health Organization) (Witek-Krowiak et al. 2011; Mishra and Bharagava 2016; Saxena et al. 2017; Joshi

Table 7.1 The distribution and recommended concentration of chromium in various environments (Krishnamurthy and Wilkens 1994)

Sample type	Concentration
Natural soils	5–1000 mg kg^{-1}
	5–3000 mg kg^{-1}
	5–1500 mg kg^{-1}
	30–300 mg kg^{-1}
	Trace to 5.23%
Serpentine soils	634–125,000 mg kg^{-1}
World soils	200 mg kg^{-1} (mean)
	100–300 mg kg^{-1}
	10–150 mg kg^{-1} (mean 40 mg kg^{-1})
Sediments	0–31,000 mg kg^{-1}
Fresh water	0–117 μg L^{-1} (average 9.7 μg L^{-1})
Sea water	0–0.5 μg L^{-1}
Air	1–545,000 ng m^3
	100 ng m^3
Plants	0.006–18 mg kg^{-1}
Animals	0.03–1.6 mg kg^{-1}

2018). Cr (VI) pollution is of utmost concern worldwide, as it is considered extremely toxic, mutagenic, and carcinogenic for living organisms. For the last 15 years, chromium has been classified among the 20 most lethal environmental contaminants (Chrysochoou et al. 2012).

Effluents of manufacturing industries such as textiles, tanneries, electroplating, tanneries, paint, etc., contains large percentage of Cr(VI) (Mohapatra et al. 2017; Kishor et al. 2019). These industries are releasing their effluents continuously in their surroundings, which is a leading threat to environmental safety. Because chromium is a nondegradable pollutant as it persists in the environment (Ran et al. 2016).

Hexavalent chromium can cause severe infections such as, skin and lung cancers, hepatic diseases and bronchial tract infections, etc. (Ali et al. 2016). However, trivalent chromium is less toxic and exists in oxides and hydroxides which is insoluble at pH >5 (Mohapatra et al. 2017). As a result, Cr(III) is not capable of entering into the cells and removed easily. Hexavalent to trivalent chromium reduction can be achieved by physiochemical, electrochemical, and biological processes (Habibul et al. 2016). Several physiochemical techniques are used such as chemical precipitation, membrane separation, solvent extraction, and ion exchange (Witek-Krowiak et al. 2011). These methods are inadequate and ineffective for chromate removal, due to high cost and energy consumption, incomplete removal and formation of other toxic compounds.

Cr(VI) removal has also being carried out through biological techniques. These techniques are environment friendly, cost-effective, safe, and free from toxic side products formation (Eccles 1995; Shakoori et al. 2000). Various studies have investigated plants, yeasts, fungi, and bacteria for remediation. Microbes are being exploited for beneficial purposes. Bacteria develop different mechanisms to overcome metal toxicity such as intracellular and extracellular reduction of Cr(VI), metal efflux, DNA repair enzymes, and detoxification enzymes for reactive oxygen species (ROS) (Thatoi et al. 2014). Heavy metal ions accumulate in bacterial cells in both soluble as well as in particulate form (Devi et al. 2017). Microbes convert toxic hexavalent chromium into less toxic trivalent chromium either by direct method that involves enzymatic reduction or by indirect process that consist of formation of complex compounds with metabolites (Bento et al. 2005; Pei et al. 2009; Soni et al. 2013; Chandra et al. 2011). Several bacteria such as *Agrobacterium*, *Bacillus*, *Deinococcus*, *Enterobacter*, *Escherichia*, *Pseudomonas*, *Shewanella,* etc., are reported to show high Cr(VI) reduction potential (Thatoi et al. 2014). Cr(VI) reduction greatly depends on temperature, pH, and chromium salt concentrations (Wani et al. 2018).

The process of removal of heavy metals through biological materials is termed as biosorption. This technology is very operative for detoxification of toxic industrial effluents. Agricultural wastes are efficient biosorbent materials and have low cost such as rice husk, exhausted coffee, peat moss (Dakiky et al. 2002), rice hulls and soybean hulls (Marshall and Champagne 1995; Tarley and Arruda 2004), and wheat bran (Iqbal et al. 2002). These biosorbent materials are used in combination with Cr(VI) reducing bacteria for efficient removal of chromate from environment.

Thus, this chapter describes the properties of tannery effluents, hexavalent chromium as major pollutant, health risks, and effect of Cr compounds on the biosphere and remediation of tannery effluents by biological and nonbiological methodologies. The purpose of this chapter is to give complete information about tannery effluents and related issues that are required for further research and development.

7.2 Production and Properties of Tannery Effluent

In Pakistan, tanning industries are the leading cause of pollution due to disposal of unprocessed wastes in water bodies and on land. Developing countries have been observed with an increase in leather production as compared to developed nations. Pakistan has gained an increase in leather export from US$ 672 million to US$ 1.13 billion, indicating a cost increase of 68% in a 5-year span (2002–2007) (Haydar and Aziz 2009). Currently, there are about 2500 leather manufacturing units in Pakistan. From year 1999 to 2015, number of tanning units have raised from 529 to 800 (Padda and Asim 2019; Bharagava et al. 2018). In tanning process, animal hides are transformed through various chemical reactions to leather. Four major steps are involved for production of leather i.e., beams house operation (pre-tanning), lanyard processes, retaining, and finishing (US EPA 1986; Tunay et al. 1995; Cooman et al. 2003; Saxena et al. 2017) (Fig. 7.1). The hide is processed through various chemicals such as NaOCl, NaOH, H_2SO_4, chlorides, enzymes, lime, formic acid, chlorobenzene, ammonium salts, kerosene, tenso-active compounds to remove fat, meat, and hair. The hide is then subjected to mineral salts, chromium [Cr(III)], and dyes to leather. Thus, effluent generated has a large quantity of Cr(III), sulfates, sodium, and chlorides. However, the end products of each step produce different kind of waste materials and concentration may vary (Tunay et al. 1995). Basaran et al.

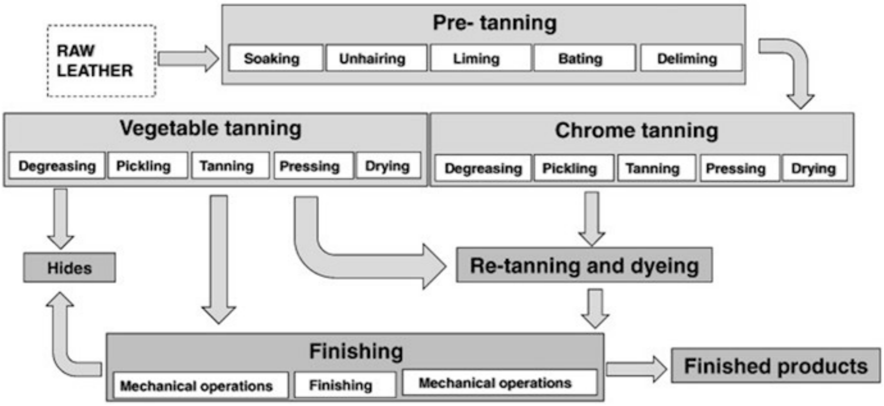

Fig. 7.1 Flow sheet of leather tannery industry (Lofrano et al. 2013)

(2008) and Saravanabhavan et al. (2004) described similar procedures for leather tanneries situated in Turkey and India, respectively.

7.3 Environmental Pollution and Health Hazards of Tannery Effluent

Anthropogenic activities are causing heavy metal contamination in the environment globally and are one of the primary sources of metal ion uptake in the food chain leading to serious diseases. In Pakistan, heavy metal contamination has created a serious situation regarding human health, environment, and economy. The disposal of untreated industrial effluent from leather tanneries has caused an accumulation of chromium (Cr) compounds in the areas near tanneries. Previous studies by Pakistan EPA has reported Cr values in the tannery waste, which are significantly higher than the safe limits established by nation standards (EPA 1990). Tannery wastewater is a potential noxious waste. It has created severe ecological problems that are linked to high concentration of chrome together with its rich coloration and high chemical oxygen demand (COD). Cr(III) is extensively utilized as tanning agent in leather tanneries as it forms complex compounds with proteins and amino acids (Song et al. 2000). This trace element is necessary for normal development of human and animals. In the pure state, Cr(III) has no harmful effect. When present in large quantity, it shows little toxic effect. Generally, Cr is not completely integrated into the leather and comparatively large quantity of Cr is discharged into the effluents. About 2% Cr is present in hide dust in the effluent and other wastes. Effluents from leather tanneries end up in the surroundings and large quantity of Cr is accumulated that are converted into more toxic and insoluble form with time because of complex structures formation with hydroxyl ions (Khan 2001).

Hexavalent chromium compounds are responsible for both acute and chronic toxicity. The interaction of Cr(VI) compounds by contact, ingestion, or inhalation causes severe illnesses such as eczematous and allergic skin reactions, dermatitis, damage to the nasal septum, mucous and skin ulcers, bronchial infections, allergies, hepatocellular deficiency, inflammation of stomach and intestines, etc. (Khan 2001; Chandra et al. 2009).

7.4 Cr(VI) as a Major Pollutant in Tannery Effluent

Environmental damage caused by tannery discharge has created a critical problem in Pakistan and signifies a technical challenge for an efficient and safe cleaning process. Chromium, a brittle,, and shiny metal is present in environment in combined form around 0.1–0.3 mg/kg of earth's surface. It exists in several oxidation states (−2 to +6) and the most stable are Cr(III) and Cr(VI) (Molokwane et al. 2008).

Cr(III) solubility is affected by the formation of oxides and hydroxides. Chromium is mainly employed in the metallurgy industry, particularly stainless steel production. Other Cr salts are used for manufacturing of pigments, leather tanning, metal finishing, etc. Tanned hide is approximately 80–90% made from chromium compounds (Papp 2004). Discharged effluents from tanneries contain about 40% of Cr as Cr(III) and Cr(VI). For each 200 kg of hide, more than 600 kg of waste is produced by a tannery (Khan 2001). Cr chemicals have also been used for the production of metal castings and mortars, refractory bricks, and as wood preservative.

Conversely, the US Environmental Protection Agency (US EPA) has prohibited the use of Cr(VI) compounds as a wood preservative regarding health issues. Because of wide applications, huge amount of Cr wastes is released into the environment each year. In 2003, US EPA declared about 32,589.6 metric tons of Cr compounds was disposed of and half of the quantity was landfilled in the surroundings (US Environmental Protection Agency 2005). Potable water guidelines by the WHO states 0.05 mg/L as the maximum permissible limit for total chromium. Cr is hazardous, but also spreads fast over aquatic systems and underground waterways. Consequently, Cr has been recognized as toxic environmental pollutant by US EPA (Narayani and Shetty 2013).

7.4.1 Impact of Chromium Compounds on Environment

Chromate is present naturally but anthropogenic activities give rise to Cr(VI) pollution in the environment. Natural sources contribute 54,000 tons of chromium. Studies showed that atmospheric Cr comes back to soil and water bodies by rain. Cr estimated time to reside in the atmosphere is less than 10 days (Agency for Toxic Substance and Disease Registry (ATSDR) 2015). Chromate present in soils can seep into surface water because of its highly soluble and mobile nature (Coetzee et al. 2018). It is a common practice to irrigate agricultural land by wastewater. Tannery effluents has large content of valuable nutrients, however it also contains toxins such as Cr that might damage soil quality and crop production (Alvarez-Bernal et al. 2006). High percentage of Cr in soils can prevent germination of seeds and growth of seedling. The toxic effects of Cr are less apparent on seed development than on growth of seedling. Barley seeds were able to germinate in soil under chromate stress of 100 mg/kg. However it showed slow growth due to Cr(VI) inhibition of diastase that is necessary for mobilizing the starch reserved for early growth (Zayed and Terry 2003).

In plants, the toxicity of Cr is greatly dependent on ionic species of element. Hauschild (1993) analyzed the effect of Cr(VI) toxicity in barley and rape plants provided in hydroponic culture. Cr(VI) and Cr(III) were supplied in the range of 0–100 mg/kg. When chromate (100 mg/L) stress was applied to plants, up to 3000–5000 mg/kg of Cr(VI) was accumulated and was up to 300–400 mg/kg when Cr(III) (100 mg/L) stress was applied in hydroponic culture. These high levels of chromium caused leaf chlorosis, reduced root and shoot growth, stimulation of chitinase activity, and low levels of water content in leaves (Zayed and Terry 2003).

7.4.2 *Health Hazards of Chromium Compounds*

A characteristic feature of chromium is its environmental mobility and consequently is a cause of environmental risk. Cr(VI) belongs to group A human carcinogen due to its mutagenicity, carcinogenicity, and teratogenicity nature in plants, animals, and humans (Narayani and Shetty 2013) (Fig. 7.2).

The ingestion of Cr(VI) leads to severe illness and can even causes death. Oral toxicity (LD_{50}) of Cr(VI) was reported to be 50–100 mg/kg and for C(III) 1900–3300 mg/kg in rats (NIOSH 1977). Cr(VI) ions readily solubilize in water and hence can pass through the cell permeability barriers (Thacker et al. 2006). In the living cells, oxyanions of heavy metals has impact on the metabolism of structurally associated nonmetals. Hexavalent chromium toxicity is linked to its capability to induce oxidative stress and damage DNA in cells (Reynolds et al. 2009). Previous studies have extensively described the development of oxidative stress that led to membrane damage for example, loss of membrane potential or inhibition of electron transport chain (ETC) both in prokaryotes and eukaryotes.

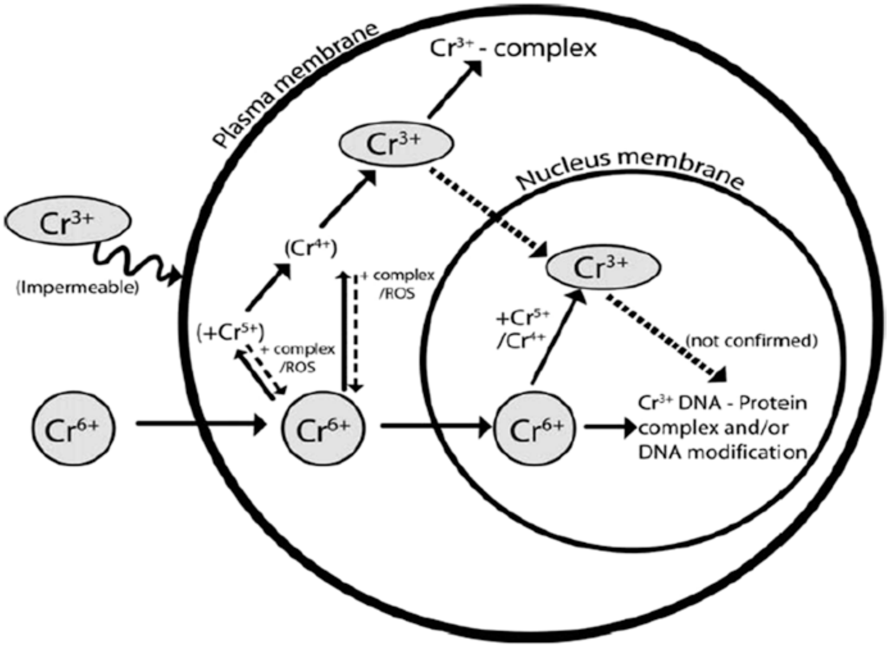

Fig. 7.2 A schematic diagram showing mutagenicity and toxicity of chromate ions (Narayani and Shetty 2013)

Hexavalent chromium is a carcinogen based on studies regarding respiratory cancer in individuals that are occupationally exposed to it (Mishra and Bharagava 2016; Chandra et al. 2011; Langard 1983). A temporary exposure levels of Cr(VI) beyond maximum contaminant level can lead to skin irritation or ulceration also called as chrome holes. Whereas, long-term exposure beyond maximum contaminant level can contribute to nerve tissue damage, kidney circulation, damage to the liver, and death (Kotas and Stasicka 2000). Individuals exposed to Cr(VI) could also suffer from nasal septum lesions. The improper waste disposal, poor storage, and leakage have made chromate as one of the most commonly recorded pollutant at waste areas (Narayani and Shetty 2013).

7.5 Nonbiological Methodologies for Effluent Remediation

Environmental protection agencies have concerns about waste treatment. Industrial effluents have bad impact on the surroundings, if strict regulatory standards are enforced then it will surely contribute to increase waste removal costs. Therefore, effluent processing is essential for long-term organization benefit. For controlling Cr pollution in countries where leather is produced at large-scale, tannery effluent treatment has become a critical issue, because of its substantial toxic content. Various leather fabricating activities and procedures bring about the generation of different types of fluid discharge. A difference in fluid volume will cause a significant effect on toxin concentrations (Springer 1994; Song et al. 2000).

Usually, tannery effluents containing high concentration of Cr (VI) compounds are processed by different physiochemical approaches for example, ion exchange, reduction, adsorption, precipitation, and electrodialysis and reverses osmosis that is expensive and has other disadvantages. These disadvantages include high reagent consumption, partial metal removal, energy requirements, and production of toxic sludge. Moreover, the majority of these strategies has some limitations and only applied at high/moderate concentration of heavy metals as compared to low concentrations (1–100 mg/Z) (Addour et al. 1999; Narayani and Shetty 2013).

Few of these methods are described below;

7.5.1 Chemical Precipitation

Chemical precipitation is a commonly used technique for removal of heavy metals from waste water. In this technique, dissolved pollutants are transformed into insoluble compounds, thus enabling subsequent removal of contaminant from the effluent by physical methods, for example, filtration (NEESA 1993). In precipitation process, precipitants particles (also known as flocculants and coagulants) size is increased by aggregation. The treatment process is directly dependent on alkalinity and pH of effluent as this will determine the amount of chemical that will be used for metal removal. Generally, sodium hydroxide or lime is used to precipitate heavy metals in water in neutralization process. But this process is not effective (incomplete precipitation) particularly when complexing agents are present (EPA 2000; Xu and Xu 2008).

For many years, chemical precipitation has been utilized as a prime technique for heavy metal removal. Groundwater contaminated with heavy metals has been remediated by chemical methods in column and pilot scale experiments. In one such analysis, calcium carbonate and granulated lime were used as coagulants (Lee et al. 2007). Moreover, a few researchers have created and specifically utilized 1, 3-benzenedaimidoethathiol dianion (industrially known as Metx) that irreversibly binds metals in aqueous solutions. In an investigation by Matlock et al. (2002), Metx showed more than 90% removal of toxic metals from acid mine wastes. Precipitation with sulfide is described to be one of the most effective processes. This is a due to its low solubility to destabilize solvent complexes. Regardless of the simplicity, this process is not suggested for use since lethal compounds could be discharged in acidic pH, subsequently leads to great risks in case of occurrence of accidental discharge or over dosage.

The best alternative recommended to conventional sulfide treatment is dithiocarbonate precipitation (Metalsorb 2004). Metals chemical precipitation methods have low costs and could be done by a pH alteration. Irrespective of these advantages, compound precipitation of metals in water still has few limitations such as production of large volume of sludge, leading to additional up to 50% effluent disposal costs (EPA 2000). Each dissolved heavy metal consists of different pH level for hydroxide precipitation. This procedure requires corrosive chemicals, therefore causing safety concerns (EPA 2000; Metalsorb 2004).

7.5.2 Ion Exchange

A reversible chemical reaction in which the ions from wastewater are exchanged by a similar charged species attached to an immobile solid particle. These exchanged particles are either synthetically manufactured resin or naturally present inorganic salts. This process is primarily similar to biosorption therefore the latter is known to work mainly on basis of ion exchange. Ion exchange mostly uses hydrocarbon-derived polymeric resins (Volesky 2003). This method has been effectively used for removal of heavy metals from waste water. Vaca et al. (2001) have described the interactions of chromium, cadmium, and lead, while competing for ion exchange active sites in naturally present clinoptilolite. Their investigation showed efficient removal of dissolved metals within 18 h in batch reactors, with the percent removal of more than 95% in acidic pH.

7.5.3 Reverse Osmosis

Reverse osmosis consists of a membrane that functions as a molecular filter to eliminate 99% of all dissolved heavy metals in a solution. In this procedure, the water goes through the film while the dissolved and particulate compounds are filtered out. This procedure is very efficient for ionic species removal from aqueous solutions. The subsequent by-product solutions make it more feasible for effective recovery of heavy metals. Regardless of the adequacy, these membranes are generally expensive. This technique is costly due to the use of elevated pressure, which makes it sensitive to working conditions.

An important advantage of reverse osmosis as compared to other effluent treatment systems is the capability to reduce the other ionic pollutant concentrations as well as dissolved organic compounds (Volesky 2003; Pawlak et al. 2005). Reverse osmosis has been used in small and large-scale experiments for heavy metal removal. Pawlak et al. (2005) conducted a study in which they checked reverse osmosis membrane module for removal of total arsenic concentration in feed water over a period of 30 days. The concentration of arsenic was reduced from 60 ppb on average to 1 ppb in the treated water.

7.5.4 In Situ Chemical Sorption

In situ chemical sorption (ISCS) is also a significant method for immobilization of Cr(VI). Activated carbon displays a significantly high adsorption capability for Cr (VI) with two mechanisms of adsorption and for other inorganic compounds. Firstly, Cr(VI) ions are adsorbed on the inner carbon surface, subsequently reduced to Cr(III), later these Cr(III) ions move to outer carbon surface (Mohan and Pittman Jr 2006). GAC (granular initiated carbon) in permeable reactive barrier (PRB) systems is extremely appropriate for hexavalent chromium removal from ground waters (Han et al. 2000). If treating naturally occurring zeolites with cationic surfactants, they can gain a positive charge on its surface, bringing about an enhanced sorption affinity for anionic metals, such as chromate. They are known as surface-modified zeolites (SMZs) and can be effectively used for chromate immobilization. PRBs filled with SMZ have been successfully used for remediation of a Cr(VI) polluted aquifer.

Another effective material for chromate ions adsorption from solutions is unrefined tamarind fruit shells (CTFS) and pretreated with hydrochloric acid. Moreover, peat has been used in commercial applications for reduction and removal of chromate from polluted groundwater (Theologou et al. 2013). Ferrous materials can also be utilized for ISCS such as mixed magnetite and maghemite nanoparticles. The use of magnetite-maghemite nanoparticles is an efficient method for chromate adsorption from aqueous solutions and can also be used for treating ground water (Chowdhury and Yanful 2010). They also demonstrated that under controlled (acidic) pH conditions, the chromate ion take-up ranges between 96 and 99%.

7.5.5 Electrochemical Technique

Electrochemical techniques give a different approach for remediation of Cr(VI) contaminated sites as it represents both electrical and chemical reactions simultaneously. Electrochemical treatment procedures have considered well due to their adaptability and ecological compatibility, which makes the removal of heavy metals from solids, liquids, and gases possible. Actually, the fundamental reagent is the electron, which is a clean reagent (Barrera-Dıaz et al. 2003). Electrochemical Cr (VI) removal strategies can be utilized in various ways depending upon the electrode material, pH of the aqueous solution, and the intensity of the current density employed. In this way different chemical reactions can occur simultaneously on electrode surface or in the aqueous solution (Barrera-Díaz et al. 2012). Electrochemical treatment was considered as rapid, need few chemicals, giving high removal and selectivity of metals, and produce less secondary compounds. Conversely, this technique requires high initial capital cost and production of spongy deposits (Madhavi et al. 2013).

7.6 Biological Methodologies for Effluent Remediation

Immensely growing population, industrialization, and deforestation have led to serious ecological problems. One of them is improper waste disposal of toxic effluents of industries into the environment. These toxic effluents mainly consist of complex mixtures of heavy metals that greatly affect living beings. Cr is major heavy metals chemical toxin, present in effluents of paint, textile, dying, and leather industries. Manufacturing and industrial activities discharged more than 0.17 million tons of Cr waste in the biosphere. Due to the relatively less toxic nature and thermodynamic stability of Cr(III) than Cr(VI), discharge of tannery effluents in water bodies and on land has created high levels of Cr (30,000 mg/kg or more) (Naidu et al. 2000).

Cr is one of the micronutrient essential for proper growth and development of human body. However, exceeding a certain limit has led to various health issues. Chromium is considered toxic in its hexavalent form and can cause skin ulcers. Prolong exposure can possibly lead to lung cancer and asthma. Hence, the regulatory authorities have emphasis on rehabilitation and remediation of Cr polluted sites (Kamaludeen et al. 2003; Chandra et al. 2009). Various strategies have been developed for removal of heavy metals from the environment. Conventional remediation treatment processes for heavy metals removal includes flocculation, chemical precipitation, evaporative recovery, coagulation, electrodialysis, floatation, reverse osmosis, nano-filtration, ion exchange and ultrafiltration, etc. These procedures are effective, however, high chemical and energy requirement makes them inefficient for remediation of polluted areas. Moreover, production of highly toxic by-products and sludge makes them even more ineffective. Therefore, environment friendly, economical, and effective strategies are needed which can reduce chromate pollution in the surroundings.

Bioremediation is the biological approach to degrade heavy metals using indigenous microorganisms (Xie et al. 2010; Bharagava et al. 2014; Raman et al. 2018). The fundamental principle of bioremediation is the use of microbes (mostly bacteria) for the removal or transfer of hazardous contaminants to less toxic forms. These microbes can only destroy harmful compounds when minerals and nutrients are available to them for growth and development of cells. Microbes have the ability to produce oxidized or reduced species that precipitate the metals (National Research Council 1993).

Microorganisms including bacteria, yeasts, fungi, and algae are capable of reducing Cr(VI) (Cervantes et al. 2001). Microbial reduction of Cr(VI) to Cr(III) has been extensively studied (Cheung and Gu 2007). Two different processes are followed by microbes for Cr (VI) reduction, i.e., direct and indirect reduction. The former process comprises various reductase bacteria that obtain electrons from reduced organic substrates (nucleotides, sugars, amino acids, vitamin, organic acids, or glutathione) (Ramírez-Díaz et al. 2008). While in the indirect process bacterial metabolism produced reducing agents (Fe^{2+} and HS^{-}) that causes Cr(VI) to reduce to Cr(III) (Prevot et al. 2018).

7.6.1 Bacterial Removal of Chromate Ions

Hexavalent chromium is known for its strong oxidizing ability and toxicity to living cells (Kotas and Stasicka 2000). Bacteria can survive and grow under harsh environmental conditions. Cr(VI) toxicity causes development of various resistance mechanisms in bacteria. Several studies reported Cr(VI) resistant bacteria that gain resistivity growing in chromate contaminated sites. *Pseudomanas* sp., was the first Cr(VI) reducing bacterial species isolated by Romanenko and Koren'kov (1977) from industrial effluents. Since then many chromium reducing bacteria have been isolated from various sources and could be applied in remediation processes (Chen and Hao 1998; Chandra et al. 2011; Narayani and Shetty 2013; Coetzee et al. 2018). Many bacterial species are known to have enhanced Cr (VI) reduction potential under aerobic and anaerobic conditions (Cheung and Gu 2007).

Microorganisms, especially bacteria, exhibit various metabolic pathways that use different toxic chemical compounds as energy source through fermentation, respiration, and co-metabolism for growth and development (Ayangbenro and Babalola 2017). These resistance mechanisms includes active efflux system, formation of complexes with thiol-containing molecules, mobilization/immobilization of heavy metals, DNA repair enzymes, intra or extracellular sequestration, detoxifying enzymes for reactive oxygen species (ROS), and transformation of toxic heavy metals into less toxic compounds (Fig. 7.1) (Bento et al. 2005; Pei et al. 2009; Soni et al. 2013).

Bioremediation involves Cr(VI) to Cr(III) reduction by microorganisms and involves an additional mechanism i.e., chromate resistance. Different bacterial species are reported for chromate reduction for example, *Escherichia*, *Deinococcus*, *Arthrobacter* spp., *Bacillus cereus*, *Burkholderia* spp., *Sporosarcina ginsengisoli*, *Kocuria flava*, *and Pseudomonas veronii* (Chandra et al. 2011; Thatoi et al. 2014).

For evaluation of chromate resistant bacteria for bioremediation purposes, Salunkhe et al. (1998) took sewage sludge sample and isolated *P. mendocina* and investigated Cr(VI) reduction potential in soil microcosm study. Their investigation showed that *P. mendocina* has the potential to immobilize 100 mg/kg Cr(VI) in 8 h. After treating Cr(VI) polluted soil with bacteria, wheat seedling growth was supported without giving any toxic effects. These findings clearly exhibited the beneficial use of bacterial treatment in remediating Cr(VI) sites (Salunkhe et al. 1998; Zayed and Terry 2003). Schematic diagram of isolation of chromate resistant bacteria from tannery wastes is shown in Fig. 7.3 (Narayani and Shetty 2013).

7.6.1.1 Bacterial Biomass Used for Bulk Removal of Metal Ions

Bacteria, algae, fungi, agricultural wastes, etc. are commonly used as biosorbent materials and possess strong ability for reclaiming heavy metals contaminated sites. These materials have wide variety of sorption sites that retain metal ions and other compounds (San Keskin et al. 2018). This technology is very effective for detoxification of toxic industrial effluents. Agricultural wastes are efficient biosorbent materials and have low cost for example, straw, coconut husks, rice husk, exhausted coffee, peat moss (Dakiky et al. 2002), coconut fiber, walnut skin, waste tea (Jouraiphy et al. 2005), rice hulls, defatted rice bran, cotton seed hulls and soybean hulls (Tarley and Arruda 2004), mustard seed cakes, and wheat bran (Iqbal et al. 2002). These materials are also processed with strong alkali to increase metal binding capacity from aqueous solutions. The binding/uptake of metals to cellular compartments is usually termed as biosorption.

Biosorbents are naturally occurring ion exchange materials which mostly comprise of weak acidic and basic functional groups. Metals can be reclaimed from the matrix by treating with HCl or H_2SO_4, NaOH/complexing agents, on dead biomass or live bacteria (Coelho et al. 2015).

Plants are also capable of heavy metal removal from polluted sites. Under metal stress condition, they produce peptide molecules that are rich in cysteine amino acids for example, metallothioneins (MTs), glutathione (GSH), and phytochelatins (PCs) that readily bind and remove metal ions in biologically inactive forms. A study showed MTs over expression in recombinant bacterial cells that increase metal ions uptake, therefore giving an opportunity to develop microbial-based biosorbents for reclamation of polluted sites (Zayed and Terry 2003).

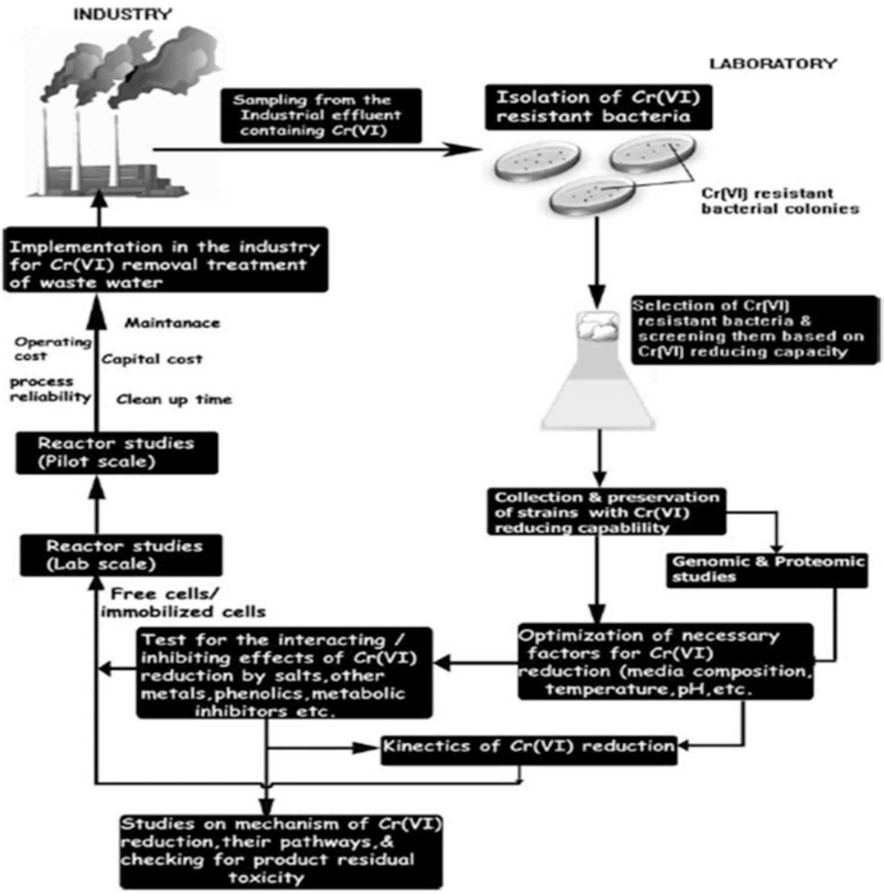

Fig. 7.3 Schematic diagram of isolation of Cr(VI) resistant bacteria from tannery wastes (Narayani and Shetty 2013)

7.6.2 *Fungal and Yeast Removal of Chromate Ions*

Fungi and yeasts have been equally known for Cr(VI) removal from contaminated environments. The beneficial characteristics of fungi are its high variability and ranging in size form microscopic molds to mushrooms. They easily grow and produce significant amount of biomass (Coelho et al. 2015). Various fungal species are reported for Cr(VI) biosorption such as *Aspergillus niger* (Srivastava and Thakur 2006), *Aspergillus oryzae* (Igwe and Abia 2006), *Trichoderma* sp., (Vankar and Bajpai 2008), *Fusarium oxysporum* (Amatussalam et al. 2011), *Aspergillus fumigatus, Aspergillus versicolor*, *Penicillium canescens* (Coelho et al. 2015), and dead fungal biomass for example, *Rhizopus oryzae, Aspergillus niger, Saccharomyces cerevisiae,* and *Penicillium chrysogenum* (Park et al. 2005). The protein molecules present on fungal cell surface comprise different functional groups that adsorb

Cr(VI) by forming chemical bonds. FTIR analysis of fungal cell wall surface showed occurrence of hydroxyl, carboxyl, amino, and carbonyl functional groups that help in the binding of chromate ions (Vankar and Bajpai 2008; Amatussalam et al. 2011).

Various studies have developed biosorbents material by using fungal strains and examined their efficiency for Cr(VI) removal. In a study, *Carica papaya* plant dry stem was used as biosorbent matrix and *F. oxysporum* cells were colonized with it. About 90% chromate biosorption was achieved using this material by the end of fifth day of incubation (Amatussalam et al. 2011). Singh et al. (2016) established *Aspergillus flavus* biosorbent material, incorporated with ferrous ions, improved removal of Cr(VI) along with the adhesiveness of biosorbent material. A study was performed with fungal strains *A. flavus* and *A. niger* associated marine seaweed to investigate for Cr(VI) resistance and accumulation. The results showed that both strains were capable of accumulating more than 25% of Cr provided to them. *Aspergillus flavus* showed maximum accumulation potential (Gupta et al. 2000). Other organisms such as *Hypocrea tawa* (Morales-Barrera et al. 2008) and *Trichoderma inhamatum* (Morales-Barrera and Cristiani-Urbina 2008) were reported for chromate reduction after biosorption process (Jobby et al. 2018). Fungal removal of hexavalent chromium generally depends on anionic biosorption.

However, other studies have suggested the use of fungal mycelia as biosorbent material that involves adsorption-coupled reaction, adsorbing Cr(VI) on biomaterials followed by reduction through non-enzymatic reactions to trivalent chromium with help of electron donors contained by the biomaterial (Park et al. 2007). Cr(VI) reduction by yeast was studied by Martorell et al. (2012). They isolated *Pichia jadinii* M9 and *Pichia anomala* M10 yeast strains from dye industry discharge. These strains also transformed Cr(VI) into Cr(III) by chromate reductase activity. Mahmoud and Mohamed (2017) showed Cr(VI) biosorption by utilizing biomass/polymer matrices beads (BPMB). They synthesized BPMB by immobilizing *Saccharomyces cerevisiae* biomass in 3% alginate extract. Approximately, 85% Cr(VI) reduction was achieved at 200 ppm initial chromate concentration and optimized cultural conditions (Jobby et al. 2018).

7.6.3 Algal Removal of Chromate Ions

Algal biomass are also used for biosorption of Cr(VI) from aqueous solutions such as tannery effluents, contaminated wastewaters, etc. Cr(VI) remediation is achieved by occurrence of functional groups for example, hydroxyl, amino, sulfate, and carbonyl in association with specific molecules phytochelatins, metallothioneins, guluronic acid, alginates, and sulfated polysaccharides solutions. Algal cell surface adsorbs Cr(VI) and then accumulates it intracellularly (Sen and Dastidar 2010; Jyoti and Awasthi 2014). Several biosorbent materials has been established and assessed for maximum Cr(VI) removal by applying biomass of *Euglena*, *Cladophora crispata*, *Dunaliella* sp., *Laurencia obtuse*, *Pachymeniopis* sp., *Scenedesmus incras-*

satulus (Ahluwalia and Goyal 2007), *Ceramium virgatum* (Sari and Tuzen 2008), *Spirogyra* sp., (Gupta et al. 2001), *Nostoc linckia* (Mona et al. 2011), *Spirulina* sp., (Rezaei 2016), *Chlorella vulgaris* (Sibi 2016).

Different studies are reported for batch cultures optimization of different physiochemical parameters (pH, temperature, adsorbent concentration, agitation time, initial chromate concentration, adsorbent dose, and contact time) to achieve maximum chromate adsorption on algal biomaterials. *Cladophora* biomass showed maximum Cr(VI) accumulation i.e., 72% after 15 min, it was followed by *Chlorella vulgaris* 34–48%, and *Selenastrum* with 39% chromate accumulation. *Spirulina* biomass accumulated up to 82.67% of Cr(VI) under optimized conditions at 10 mg/L initial chromate concentration (Rezaei 2016; Jobby et al. 2018).

7.6.4 Phytoremediation of Chromate Ions

Chromium is the second most abundant heavy metal that enters into the agricultural systems by application of Cr contaminated wastewater (Saxena et al. 2017; Gupta et al. 2018). Phytoremediation technique includes the use of plants to remediate heavy metal polluted water and soils through biochemical degradation, uptake, accumulation, or sequestration of heavy metals. The vascular plants are capable of up taking heavy metals, accumulate, and store large amounts through their root systems. The uptake of chromium contaminants in plant has been conducted through various laboratory studies and small-scale field trials (Fruchter 2002). The metal tolerance is greatly influenced by plant species and genotype.

Phytoremediation of Cr(VI) has been investigated in several plants such as *Agave lechuguilla*, *Atriplex canescens*, *Larrea tridentata, Thuja* orientalis, and *Pinus sylvestris* (Madhavi et al. 2013). Romero-González et al. (2006) used *Agave lechuguilla* biomass for chromate biosorption. Cr(VI) absorption was maximum at pH 2.0 either due to electrostatic attraction of positively charged ligands for example, protonated amines to Cr(VI) oxyanions or through Cr(VI) to Cr(III) reduction, consequently resulting in the binding of Cr(III) to the biomass (Romero-González et al. 2006; Madhavi et al. 2013).

Plants are reported to produce specific enzymes that have similar function as chromate reductase produced by bacteria and mediate in chromate reduction (Lytle et al. 1998). Early efforts for phytoremediation of Cr(VI) contaminated sites of Ranipet Tanneries in Tamil Nadu was performed with *Sorghum* by Revathi et al. (2011). They examined the effect of chromate ions on content of chlorophyll and biomass. Increased concentration of Cr(VI) showed significant reduction in plant biomass. The plant biomass was effectively increased by supplementation of vermicompost to the polluted soil, creating more space for accumulation of chromium. Various other plants have been reported for their ability of accumulating Cr includes *Barringtonia acutangula* (Kumar et al. 2014), *Callitriche cophocarpa* (Jobby et al. 2018), *Pterocarpus indicus*, *Jatropha curcas* (Mangkoedihardjo et al. 2008), *Jasminum sambac, Jasminum grandiflorum, Polianthes tuberosa, Nerium oleander,* and *Helianthus* sp. (Jobby et al. 2018). *Callitriche cophocarpa* was reported as best Cr(VI) accumulator showing 27 times greater chromate concentration in fresh shoots as compared to the older ones (Jobby et al. 2018).

Phytoremediation is a low energy, inexpensive, and eco-friendly technique. It causes fewer disturbances in soil ecosystem. It prevents excavation and is generally acceptable and easily maintained. However, this technology is slow and time consuming due to slow growth rate of plants. After remediation, plant biomass needs proper disposal. A change in agro-climatic conditions directly affects phytoremediation. The pollutants can enter soil again by litter formation of these heavy metal accumulating plants. The solubility of contaminants may be increased by root exudates of hyper-accumulating plants and led to dissemination of heavy metals into the soil. Therefore, to improve and make phytoremediation a sustainable technology, plants with high growth rate are required with extensive root system for accumulating high concentration of pollutants. These plants should be able to produce large quantity of biomass and along with that recombinant technology could be used to engineer common plants with hyper accumulating genes (Khan et al. 2009).

7.7 Emerging Trends and Future Prospects

Biotechnological approach such as in situ remediation is applied to reduce or eliminate toxic heavy metals that have led to environmental hazard and risks. In situ remediation involves direct inoculation of microbes and reagents into the polluted aquifer and is becoming progressively a common technique. The cost effectiveness, simplicity of procedure, and least interference of the site give further advantage for the application of this technique. The removal processes that utilize permeable reactive barriers is also gaining acceptance. No single technique is adequate for the removal of majority of the pollutants that might exist at a site or to accomplish compliance with cleanup standards. To accomplish the goals, the use of treatment train strategy is frequently required.

For instance, inorganic reductants might be applied for mass removal of chromate contaminants, followed by the use of anaerobic bioremediation and/or to additionally check natural reduction. This strategy is gaining commercial acceptance and application, particularly at complex sites. On commercial ground, new reagents/chemicals are also added for both bioremediation and inorganic pathways. In various remediation systems, nanotechnology is applied particularly nZVI that is rapidly developing field and an effective approach for reclamation of chromate polluted environments. These materials are costly as compared to conventional materials. However, using nanoparticles in areas where conventional material may not be applied such as fractured rock aquifers. Other nanoparticles such as carbon nanotubes were used for reduction of hexavalent chromium that showed very promising results (Gu et al. 2013). Different reports are available on combination of bioremediation and electro-kinetics with significant outcomes (Fonseca et al. 2011).

Hexavalent chromium reduction can also be achieved by immobilizing microbial cells combined with nanotechnology such as, C-nanotubes impregnated into calcium alginate, significantly improved Cr(VI) reduction and enzyme stability. Nanomaterials donate electrons in enzymatic hexavalent chromium reduction and immobilization (trivalent chromium precipitates) can likewise be applied at chromate contaminated sites for remediation purposes (Igiri et al. 2018).

7.8 Conclusion

The use of biological systems for example, microbes and plants for remediation of Cr(VI) polluted sites is significantly developing and has proven a considerable progress in situ, further combined with field trials at various agro-climatic zones all over the world. Biosorption have been established as an eco-friendly, efficient, and cost-effective technique for reclamation of Cr(VI) polluted environments. Bacterial, algal, fungal, and plant biomass are considered effective for hexavalent chromium transformation. This chapter provides a detailed understanding of Cr(VI) removal through various processes. Therefore, helping in improving current technologies to be more proficient for Cr(VI) remediation.

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Chapter 8
Photocatalysis as a Clean Technology for the Degradation of Petrochemical Pollutants

Zakhele (Zack) Khuzwayo and Evans M. N. Chirwa

Abstract Photocatalysis as a technology does satisfy the criteria as a clean technology in application and is suitable for the degradation of petrochemical pollutants. An ideal photocatalyst is expected to conform to properties of photoactivity, biological and chemical inertness, stability toward photo-corrosion, suitable for visible or near UV light energy harnessing, be low cost and be nontoxic in nature. The high stability of TiO_2 allows diverse applications such as in electro-ceramics, glass and in photocatalytic degradation of chemicals in water and air. The oxide particles can be used in the form of suspensions in slurry reactors as well as thin film coating agents. The suspended photocatalyst has been demonstrated to be very efficient degrading different classes of organic compounds. The major concern of the suspended photocatalyst system is the inability to reclaim the semiconductor catalyst in suspended slurry-type applications. This drawback has been addressed in various ways through innovative developments, which are specifically aimed at addressing this issue.

Keywords Photocatalysis · Photoactivity · Titanium oxide · Petrochemical pollutants · Degradation · Clean technology

8.1 Introduction

In modern society, one of the biggest commercial global industries is the petroleum industry, also commonly referred to as the oil and gas industry. The petroleum industry constitutes of many commercial products, including gasoline, natural gas,

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naphtha, fuel and lubricating oils, asphalt, paraffin wax, kerosene, and many more chemicals that are produced from petroleum. These chemicals are applied in the manufacture of a large number of consumer products from different sectors, such as the pharmaceuticals, electronics, motor vehicle, health care, household, and home-based manufacturers among others. Petrochemicals are so versatile that they are found in many of the facets of the human environment, these include medicine (where they are used in the production of resins, films, and plastics) (Hess et al. 2011; Frumkin et al. 2007), food (where they are used in the manufacture of food preservatives) (Neff et al. 2011), agriculture (where they are used in plastic sheeting, in pesticides, and fertilizers), household products (where they are used in many ways in the forms of films, rubbers, fibers, and plastics).

It is apparent from the above information that the petrochemical industry performs an important function in the betterment of human society through activities applied in diverse sectors. The major concern proceeding the utilization of the petrochemical functions and the end-user products is their removal from the environment once the many consumer cycles have run their course. Petrochemical industrial activities and the waste associated with it result in significant amounts of harmful substances being transferred to the environment through liquid waste discharges, solid waste and through the atmosphere (Mechhoud et al. 2016; Chen et al. 2014). The harmful petrochemical pollutant substances can pose serious risks to human health and wildlife through different exposure (Álvarez et al. 2016; Haghollahi et al. 2016; Zolfaghari et al. 2016; Hu et al. 2013; Zhong and Zhu 2013). There have been many documentations of exposure to petroleum product's harmful substances leading to severe health conditions such as organ and tissue damage in the form of liver, nerve, birth defects, cancer, asthma, brain and hormonal disorders among many more (Bustillo-Lecompte et al. 2018; Axelsson et al. 2010; Belli et al. 2004; Luginaah et al. 2002; Lin et al. 2001a, b).

Environmental contamination by petrochemical pollutants from industrial chemical plant activities most predominantly occurs through effluent discharges in the form of wastewater. This effluent is formally referred to as industrial discharge and constitutes of the waste liquid matrices produced in the chemical plant's processes, which contains industrial production materials, intermediate compounds products, and the toxic substances produced as part of the production process. The petrochemical industry boasts a diverse repertoire of products that are produced using many different reaction schemes. For this reason, industrial processes discharge wastewater that is made up of a huge range and variety of chemical components, some of which may be resistant to natural degradation processes (Liang et al. 2019; Varjani et al. 2017; Xiaoqiang et al. 2019).

8.2 Petrochemical Pollutants

Petrochemical pollutants are chemical contaminants that are typically present in effluent matrices discharged from industrial activities associated with fossil fuels refinery processes by chemical plants. Various types of chemical plants processes are utilized in efforts to process natural materials toward reusable chemical products. Some of the natural materials converted to chemical products for commercial applications include minerals, metals, natural gases, air, water, and fossil fuel oil. Petrochemical pollutant chemical compounds specifically result from the conversion of natural gas liquids through cracking and distillation processes and through the extraction processes of crude oil. In essence, petrochemicals can be classified as compounds sourced from the hydrocarbons of natural gases and petroleum fractions.

Typical extraction and conversion process from the natural forms of these hydrocarbons toward the desired end products are complex and require many chemical reaction steps. Each of these steps results in the production of multiple and various types of chemical by-products that represent many different chemical groups. Commonly, petrochemicals can be classified into two groups. These classification groups are known as the olefins and the aromatics. Olefins, also termed alkenes, are hydrocarbon chemical species that only contain carbon–carbon double bonds, whereas the alkanes constitute of single bonds (Bruice 2004). Petrochemical olefins include chemical compounds such as propylene, butadiene and ethylene. Aromatic compounds are associated with benzene as the base compound, which has a six-carbon π system in a cyclic form (Bruice 2004). Petrochemical aromatics include chemical compounds such as benzene, xylene and its isomers, ethylbenzene, and toluene.

The above described petrochemical compounds are also referred to as primary petrochemicals; these chemical hydrocarbon molecules are further processed to manufacture petrochemical intermediates (Souza et al. 2014). The manufactured petrochemical intermediates and reaction steps process chemical derivatives produced are products of the primary petrochemical starting products and are referred to as secondary petrochemicals. The secondary petrochemical are also further processed to form daughter products; these are collectively referred to downstream petrochemicals. The term downstream simply means that the particular petrochemical compound is reactively formed later in the sequence of chemical reaction events.

8.3 Diversity of Petrochemical Pollutants

Petrochemical pollutants are sourced and can be sourced from many different hydrocarbon starting materials (primary petrochemicals) of the natural environment. The following brief description will detail some of the sources of petrochemicals that are processed toward usable end products. A subsequent acknowledgement is that due to the diversity of the petrochemical groups that are converted from the different primary petrochemicals, the refining processes generate large quantities of petrochemical wastewater, which upon discharge contaminate natural water bodies, and when discharged toward treatment facilities, the sheer complex nature of the chemical intricacies overwhelms most conventional treatment processes, and/or require large amounts of resources to treat and process to acceptable standards. This is one of the primary drivers with regard to seeking cleaner and less resource-intensive technologies in dealing with petrochemical industrial waste.

8.3.1 Petrochemicals from Downstream Products

Industrial wastewater matrices can be immensely complicated due to the high number of different chemical groups derived from the primary petrochemicals, secondary petrochemicals, and the diverse products formed from the reactions of compounds. The following discussion segment will elucidate the nature of this phenomenon by accounting for some of the products formed from downstream petrochemicals such as methane, ethylene, and benzene. The complex nature of treated petrochemical influent poses a real challenge for most conventional treatment installations, and where advanced treatment technologies are in place, the amount of resources required for the discharged product to meet standard regulation stipulated in the various legislations around the world can be costly. The vast number and the various chemical products derived from downstream reaction processes will be evaluated in an attempt to garner appreciation for the technological challenge of treating petrochemical wastewater.

8.3.1.1 Downstream Petrochemical Products from Methane

Methane is derived from petroleum refining processes in large quantities. Many petrochemical compounds from related groups can subsequently be reactively formed. Some of these products include but not limited to:

- Methyl alcohol—methane is converted to methanol (methyl alcohol) under an oxidative catalyst in the presence of oxygen molecules. Methanol is used in many industrial and commercial products as a versatile solvent. Methanol can also be further oxidized to produce formaldehyde, which is also used as a raw agent for various products.
- Unsaturated hydrocarbons—these are compound complexes that comprise of double and triple bonds. Through pyrolysis protocols and in the presence of suitable catalysts, methane is converted to unsaturated products such as acetylene ethylene and propylene. These unsaturated hydrocarbons are also the starting compounds for many other downstream products.
- Chlorinated products—Chlorinated solvents are formed from the substitution of hydrogen molecules from the methane compound. All four carbon–hydrogen bonds can be replaced to form carbon tetrachloride.
- Hydrogen—the pyrolysis of methane produces hydrogen, the primary application of this form of hydrogen is in the manufacture of ammonia gas. Ammonia is a primary starting compound in the production of many useful products, which themselves serve in the formation of different end-user products
- Carbon black—this substance is used in the pigment industry in the form of ink and in the rubber industry. This is achieved by heat stripping the hydrogen molecules from methane.

8.3.1.2 Downstream Petrochemical Products from Ethylene

Ethylene is the simplest of the olefins group, derived from the pyrolysis of naphtha. It has a carbon–carbon double bond, deeming it very reactive and easily converted to lower-end petrochemical products. It is predominantly applied in the synthesis of products such as paints and cosmetics among many more (Medianu et al. 2012). The more common petrochemical products derived from ethylene include:

- Ethyl benzene—this compound is a reaction of benzene and ethylene, the reaction takes place in the presence of a catalyst. The conversion of ethylbenzene to styrene allows the manufacture of polystyrene.
- Ethyl alcohol—this compound is the product of the hydration of ethylene. It is the solvent used in the manufacture of a large number of compounds, including acetic acid and ethyl acetate.
- Polyethylene—this compound is polymerized to form plastic materials.
- Ethylene oxide—ethylene is reactively oxidized to form ethylene oxide, which is used in the production of ethylene glycol.
- Vinyl chloride—this compound is formed directly from ethylene
- Ethylene glycol—this compound is used in the manufacture of polyester materials.
- Dichloromethane—a reaction of ethylene and chloride produces this compound.

8.3.1.3 Down-Stream Petrochemical Products from Benzene

Benzene is primary produced from naphtha through a process of aromatization, where the aliphatic hydrocarbons from the naphtha are used to produce aromatic hydrocarbons. The more common petrochemicals manufactured from benzene include:

- Chlorobenzene
- Nitrobenzene
- Ethyl benzene
- Cyclohexane
- Alkyl benzenes (linear and branched)

8.3.1.4 Down-Stream Petrochemical Products from Other Primary Compounds

Butadiene, propylene, and acetylene are the other primary chemical compounds that account for numerous downstream petrochemical compounds. The unsaturated hydrocarbons compounds propylene and acetylene are derived from natural gas, while the two carbon–carbon double-bonded butadiene is derived from naphtha.

The more common petrochemical compounds that are produced from these compounds include:

- Butadiene monomers
- Acetaldehyde
- Vinyl acetate
- Acrylonitrile
- Glycerol
- Isopropyl benzene
- Polypropylene
- Isopropyl alcohol

The compounds listed above Sect. 8.3.1 are just some of the many prominent petrochemicals that form part of most chemical plant wastewater constituents. Most of the petrochemicals listed are in a lot of cases the starting products for many simple and complex chemical compounds that are classified as pollutants.

8.4 Treatment of Wastewater and Petrochemical Pollutants

The chains of application of petrochemical compounds utilized in industrial operations are seldom confined to the chemical plants. The manufactured products take on many forms and have variety of application intended for the end users. The eventual end users include both the general public and the privatized firms. Privatized firms typically consume and/or convert the raw acquired product into secondary (downstream) products by further reprocessing these in various ways and forms, which in turn lead to the goods being accessed by the final end users, who are the general public and service provider entities. It should therefore be understood that petrochemical pollution emanating from the manufactured and consumed products exists in the natural environment, meaning that the issue of petrochemical waste treatment directly affects the whole water management cycle. Though it is imperative to stress the importance of petrochemical treatment from the primary sources, these being the oil refinery chemical plants and related facilities, the petrochemical pollutants are also found in secondary sources.

Secondary sources would be those that contribute to wastewater that is generally treated from public households and the commercial sectors. Therefore, different levels of dealing with petrochemical pollution should be recognized. Downstream-level manufactured products that are derived from primary and secondary petrochemicals are conventionally classified separately, and usually form part of larger classification group of these pollutants, one such group for example is the persistent organic pollutants (POPs). POPs are organic compounds with properties that are resistant to environmental degradation using conventional methods. To stay aligned to the subject focus of this chapter, the treatment of downstream-level manufactured products will be limited to comparative referencing with regard to treatment process analysis. The area of interest is the prospect of treating petrochemical industrial effluent using cleaner technologies.

It however should be noted that in most parts of the world, especially in the developing economies, conventional and traditional wastewater are still employed in treating petrochemical waste, without special consideration of the process required. Industrial discharged waste is approached similarly to common waste from the households and commercial environments (Naderi et al. 2017; Stasik et al. 2015; Wu et al. 2015; Viguri et al. 2002; Zheng and Richardson 1999). The analysis of traditional, conventional, and advanced wastewater treatment methodologies should form part of the narrative that promotes the application of cleaner technologies in the degradation of petrochemicals.

8.4.1 Treatment of Wastewater Pollutants

The treatment objective of the wastewater is to remove any and all contaminants that may deem the water not fit for human consumption. There are predominantly two types of wastewater treatment methods, namely, unit operations and unit processes. Methods of treatment in which physical forces predominate are called unit operations, while methods that remove pollutants by chemical or biological reactions are called unit processes (Metcalf and Eddy, Inc. 2003). Typical treatment plants combine physical, chemical, and biological methods in treating wastewater. There are different levels of wastewater treatment; these are described in Table 8.1.

Traditional water and wastewater treatment technologies are designed to deal with particulates, biological removal of pollutants and chemical contaminants dissolved in water. These methods include:

Table 8.1 Wastewater treatment process levels

Treatment level	Description
Preliminary (grit removal and screening)	Removal of solid objects and material, these are floatables, grease, sand, and more. Meant to prevent operational interference
Primary	Removal of suspended solids and organic matter
Advanced primary	Enhanced removal of finer solid particles and organic matter, with the inclusion of chemicals
Secondary	Removal of biodegradable organic matter by dissolution and suspensions
Nutrient removal	Removal of biodegradable organics, suspended solids, and nutrients
Tertiary	Removal of residual suspended solids by filtration methods, and disinfection
Advanced	Removal of remaining material from the treatment processes above, these are dependent on target compounds

- Filtration, the removal of suspended solids from the water by passing water through a porous medium; this process is completely ineffective in removing chemical pollutants.
- Sedimentation, a process that allows the flocculated or coagulated particles time to settle by gravity in a sedimentation tank. Unless the dissolved compounds are precipitated and agglomerated into the flocculants or coagulated particles, this process in mostly ineffective, and in cases where it might be effective for a single class of compounds, it would be impractical to develop a method for each of the multitude of emerging pollutants and known species.
- Flocculation, the agglomeration of particles in water or wastewater to promote settling by using high-molecular-weight materials. Most organic micro-pollutants are unamenable to flocculation.
- Coagulation, this is the process of using physiochemical methods to promote particulate settling by reducing net electrical repulsion forces between particles. This is strictly a solute-based method.
- Activated carbon absorption, this is a process used to remove low concentrations of contaminants from water that are difficult to remove by other means. Given that a suitable material is used, both adsorption and absorption are possible as a means of using surface charges and adhesion to garner particulate and chemical species of relevant properties. Activated carbon can be made extremely porous, thereby creating a very large surface area available for adsorption of contaminants

Tradition chemical processes for water treatment include disinfection as a means of removing living biological specimen that are present in natural waters and the treatment of infrastructure damaging chemical components. Disinfection in conducted in forms of

- Chlorination, hypochlorites and other forms of chloride compound complexes are used to kill harmful bacteria, parasites, and other organisms. Disinfection reactions can lead to the formation of complex intermediates that may need further treatment.
- Ozonation, is a treatment process that kills harmful bacteria and other microorganisms through an infusion of ozone. Ozone (O_3) is a gas created when oxygen molecules are subjected to high electrical voltage.
- Ultraviolet radiation, or UV application, is a disinfection process for water and wastewater treatment that involves passing ultraviolet light through water or wastewater. UV light kills microorganisms present in water. This process in advanced oxidation is called photolysis, though the intended end result in application to advanced oxidation process is different to that of traditional disinfection, the application may be the same, and the UV intensity properties may be a point of interest when applied in advanced oxidation.
- Ion exchange softening, is a process of using either natural or synthetic ion exchange resins to remove hardness from water. The resins exchange non-hardness-causing sodium ions for hardness-causing calcium and magnesium ions.

The primary physical treatment methods, such as screening and centrifugation, and secondary treatment methods, such as clarification, trickling filtration, are not intended for advanced chemical removal and do little to rid water of dissolved pollutants. Traditional physical and chemical water treatment technologies do not affect most organic micro-pollutants, and in some cases through by-product reactions, it exacerbates the toxicity of post-treatment water quality.

8.4.2 Treatment of Petrochemical Pollutants

Discussed earlier are the conventional treatment protocols for general wastewater constituents, and included is the treatment of petrochemical pollutant compounds from secondary source waste. The pertinent challenge under scrutiny is in the treatment and degradation of petrochemicals from primary sources such as the oil refinery and related industries. To obtain a better understanding of the type of waste produced from refining industry processes, a brief description of the core operation processes will be outlined. Refinery chemical plants apply a wide range of physical and chemical processes in their operational processes (Wong 2000). Refinery flow process configurations are therefore guided and determined by the composition of the source feedstock and the desired final petroleum product. Operational processing and auxiliary units in a generic refinery plant follow the treatment process steps as presented below, sourced from the EPA (1977):

Step 1: The separation process ((1) atmospheric distillation; (2) vacuum distillation; (3) recovery, gas processing).
Step 2: The petroleum conversion process ((1) cracking (thermal and catalytic); (2) reforming; (3) alkylation; (4) polymerization; (5) isomerization; (6) cooking; (7) visbreaking).
Step 3: The petroleum treatment process ((1) hydrodesulfurization; (2) hydrotreating; (3) chemical sweetening; (4) acid gas removal; (5) deasphalting).
Step 4: Feedstock and product handling ((1) storage; (2) blending; (3) loading; (4) unloading).
Step 5: Auxiliary facilities ((1) boilers; (2) wastewater treatment; (3) hydrogen production; (4) sulfur recovery).

The above listed steps should give indication to the complex nature of the oil refinery process, and also provide comprehension of the petrochemical pollutants that are produced. Various petrochemical wastewater treatment strategies have been developed in efforts to enhance conventional treatment processes in dealing with these pollutants, some of these strategies include bioelectro-Fenton reactions, biological aerated filters, and anaerobic–aerobic processes (Zhang et al. 2018; Li et al. 2018; Mattiusi et al. 2015; Yang et al. 2015; Mirzaei et al. 2013. The biological treatment process was advocated to be the more environmentally friendlier in the treatment of petrochemicals and boasted advantages such as low operational costs, small occupation, resistance to impact load, and improved efficiency (Jemli et al. 2017; Wang et al. 2016; Lettinga et al. 2001).

8.5 Advance Methods for the Treatment of Petrochemical Pollutants

The term clean technology mostly describes the processing of any material in a manner that reduces waste, minimizes environmental contamination, and requires the utilization of little to no nonrenewable resources. In chemistry terms, clean technology is mostly referred to as green technology or green chemistry, in general. Green chemistry is defined as the "design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances" (Horvath and Anastas 2007). These terms will be used interchangeably in this chapter and will essentially hold the same meaning. Green technology will be used as the expression with regard to clean technology of petrochemical pollution treatment.

There are several new technologies that have been developed aimed at treatment of petrochemical pollutants; however, most of these do not necessarily qualify for the green technology bracket. Below are some of these technologies, adapted from Balasubramani and Sivarajaseka (2018);

- Treatment by the use of wetlands (Knight et al. 1999)
- Sulfide degradation by autotrophic denitrification (Vaiopoulou et al. 2005)
- Anaerobic treatment (Macarie 2005)
- Observer-based time-optimal control of an aerobic SBR (Vargas et al. 2000)
- Enhanced biodegradation using ozonation and BAC advanced treatment systems (Lin et al. 2001a, b)

Dimoglo et al. (2004) published one of the novel works that delved into the treatment of petrochemical wastewater using the concept of clean technologies. An electrochemical reaction protocol was applied toward the removal of hydrocarbons and grease from petrochemical wastewater. The electrolytic process applied demonstrated the successful removal of oil and grease from the chemical plant discharge without the inclusion of any chemical reagents. Advances have since been made in the development of green technology that is primarily focused on the treatment of pollutants resistant to conventional treatment methods. One potential technological area that has proven efficient in achieving this feat is through the application of advanced oxidation processes (AOP) methods. These techniques utilize chemical oxidation processes to treat organic pollutants resulting in noble constituent products, achieving complete mineralization of pollutants.

8.5.1 Advanced Oxidation Processes

There are a range of AOPs reported in literature dealing with treatment of water pollutants. AOPs technologies are generally accepted to be environmental clean-up methods that are both efficient and inexpensive (Tisa et al. 2014; Vaferi et al. 2014). They include catalysis, electrochemical, Fenton's reagent, ferrate ionizing radiation, microwave, photo Fenton's reagent, and photocatalysis. Some of the processes are commercially applied to full scale while others are being tested at pilot scale and at laboratory bench levels (Khuzwayo and Chirwa 2015; Parsons 2004; Andreozzi et al. 1999; Hoffmann et al. 1995). Several other advanced oxidation technologies such as ozonation, ozonation combined with H_2O_2, and certain types of UV irradiation are currently used for disinfection purposes in the water treatment industry (Lazar et al. 2012; Lathasree et al. 2004).

Among the mentioned AOPs, heterogeneous photocatalysis has yielded the most promising efficiencies in degrading a wide range of organic pollutants in the environment. Photocatalysis is so far the only chemical method than has been demonstrated to completely mineralize organic compounds to water and carbon dioxide under ambient operational conditions. In this process, a chemically inert semiconductor metal oxide is used as a catalyst to generate oxidative oxygen species such as OH° and O° radicals. Heterogeneous photocatalysis has been uniquely useful in wastewater and water application as a result of some important features, such as (1) low operational cost and ease of operation of the method; (2) standard operating temperatures and pressure; and (3) complete mineralization achieved without by-products formed.

There are various commercially available semiconductors; titanium dioxide (TiO_2) is the most commercially used, as it offers unique principles, including (Parsons 2004):

- high activity;
- significant stability to light illumination;
- low cost;
- nontoxic and remains stable after repeated catalytic cycles

Titanium dioxide absorbs light in the visible or low-energy range (300–370 nm) of the ultraviolet regions of the spectrum. The mechanism of photocatalysis and the band gap produced has been well documented by Vinod and Anirudhan (2002), Peral et al. (1997) Hoffmann et al. (1995), and Fox and Dulay (1993).

8.5.2 Photocatalytic Degradation of Organic Pollutants

Heterogeneous photocatalysis has grown as a discipline in the last couple of decades. Its relevance to areas related to energy conservation and environmental pollutant remediation has prompted diverse developments in its applications. One of the most significant applications of semiconductor photocatalysis is the purification of water containing low concentrations of chemical contaminants (Ibhadon and Fitzpatrick 2013). The range of applicability of the heterogeneous photocatalytic concept includes surface material physics, surface sciences, photo reaction chemical and physical chemistry, chemical and environmental engineering, and material sciences (Teoh et al. 2012). Such diverse applications are mostly possible because the semiconductor element provides an environment to directly influence the chemical reactivity of a wide range of adsorbates and a means to initiate photoinduced reduction and oxidation reactions (Fox and Dulay 1993).

In the chemistry discipline, photocatalysis is defined as the acceleration of photoreactions in the presence of a catalyst. The natures of reactions that are amenable to the photocatalytic principle include oxidation, dehydrogenation, hydrogen transfer, metal deposition, water detoxification, gaseous pollutant removal, and more. The photocatalysis discipline at present is focused on the development and optimization of the technology in the removal of total organics from aqueous and gas medium systems of; chemical industry waste, water and wastewater, and environmental pollution.

An analytical review by Serpone and Emeline reported that despite many studies conducted on plenty compatible materials, no semiconductor metal oxide besides titanium dioxide (TiO_2) has been discovered that can act as a viable photoanode, with properties of the conduction and valence band edges that straddle the redox potentials of water and where rapid charge-transfer events are the rule and not the exception.

The nucleus of the photocatalytic concepts is embedded on the generation of energy bandgaps upon photon excitation of semiconductor materials. Each semiconductor material has wavelength regions at which directed photons can initiate their most active energy states. When light photons of a sufficient quantum and corresponding wavelength comes into contact with electrons on material surfaces such as semiconductors, the energy carried by the photons is absorbed, which results in the electrons moving to a higher energy state. With additional energy in spin that can overcome the energy difference, the electrons jump to the next higher orbital spin where they re-establish and settle in phase and in wavelength. The additional absorbed energy can also be relinquished by the electrons and dissipated in the form of photon energy, this results in electron descent to lower orbitals where they settle at characteristic ground energy states.

The underlining overall mechanism of the semiconductor photocatalytic process is relatively well understood and documented in scientific literature, though many intricacies about its applications remain unanswered. The champion materials to photocatalytic principle in its current format are semiconductors, those that are amenable to excitation and bandgap formation in the region of the spectrum that can be taken advantage of. These materials have requisitions of reduction potential that are less positive than their oxidation potentials. At the interface between the photocatalyst particle and the present molecules, a double layer of charge exists in metal-liquid medium junctions. This layer can be formed either by adsorption of ions or molecules or by the formation of surface bonds between the solid and the species in solution.

The photocatalytic mechanism of organic substances centers on the generation and formation of hydroxyl ($^{\circ}OH$) radicals. Free hydroxyl radicals are one of the most active nonselective initiators of photocatalytic oxidation; they are efficient hydrogen atom abstractors and attack electron-rich moieties such as complex hydrocarbon compounds (Teoh et al. 2012). Energy from UV radiation of solar sources or artificial sources is used to excite the electrons from the valence band to the conduction band; this produces electron-hole pairs. Figure 8.1 shows some of the reaction pathway platforms that are plausible in heterogeneous photocatalysis. The predominant reaction pathways for the oxidation process take place at the valence band edge of the photocatalysts surface via a positive hole formation mechanism.

The oxidation process as a whole and the efficiency of the reaction process is driven by the prevention of the electron-positive hole recombination process, which is a spontaneous and a very rapid step. The prevention of the recombination step is achieved through the reductive removal of the ejected electron at the valence band edge. This process is known as scavenging, where a scavenging molecule complex is used to occupy the loose electrons through reductive pathways generation. Oxygen molecules are typically used as the electron accepting agents, where trioxygen (O_3) molecules are formed. The trioxygen molecule is also called ozone, and this molecule is formed through the electric discharges and ultraviolet (UV) light actions. Ozone is a good scavenging molecule, due to a much higher oxidation potential than oxygen, and is used in many industrial processes as an oxidation agent.

Gerischer and Heller (1991) reported that the electron transfer to oxygen and subsequent formation of H_2O_2 might be a rate limiting step; this was also substantiated by a follow-up study conducted by Schwitzgebel et al. (1995) on the role of oxygen in photocatalysis. Hydrogen peroxide has been reported to assist in the oxidation of inorganic and organic compound by acting as a direct electron acceptor or as a direct source of hydroxyl radicals. Hydrogen peroxide can be formed via both the conduction band and valence band pathways in oxygenated matrices (Sahel et al. 2016; Lousada et al. 2015; Yamazaki et al. 2008; Hoffmann et al. 1995; Linsebigler et al. 1995). Hydroxyl radicals are formed on the surface of the titanium dioxide particle; the reaction is initiated by the valence band surface holes with titanol groups in the forms of TiOH, adsorbed water and hydroxide molecules.

Secondary radical formations from the oxidation of organic substrates increase the complexity of the photocatalytic reaction mechanism (Teoh et al. 2012; Schwarz and Dodson 1989). The secondary formed radicals can contribute to the current-doubling effect; this is one of the photocatalytic reaction possibilities indicated in Fig. 8.1. In the current-doubling effect, a single photon of light has the capacity to generate two photoelectrons, one from the excitation, ejection, and promotion at the valence band level and another that is sourced from hydroxyalkoxyl radicals in the presence of suitable organic substrates. The photocatalytic mechanism in application is not a simple and straightforward one, as it has been established that surface hydroxyl groups or adsorbed water molecules may contribute to the chemical oxidation process. This section briefly explains some of the underlining principles of the heterogeneous photocatalytic oxidation process for organic molecules in general.

Photocatalysis applications though economical and do present aspects of environmental friendliness, these aspects may qualify it in terms of green chemistry, but do not necessarily deem it a green technology without additional developments. Green technology defined earlier encompasses both the clean technology and green chemistry principles, where clean technologies mostly describe the processing of any material in a manner that reduces waste, minimizes environmental

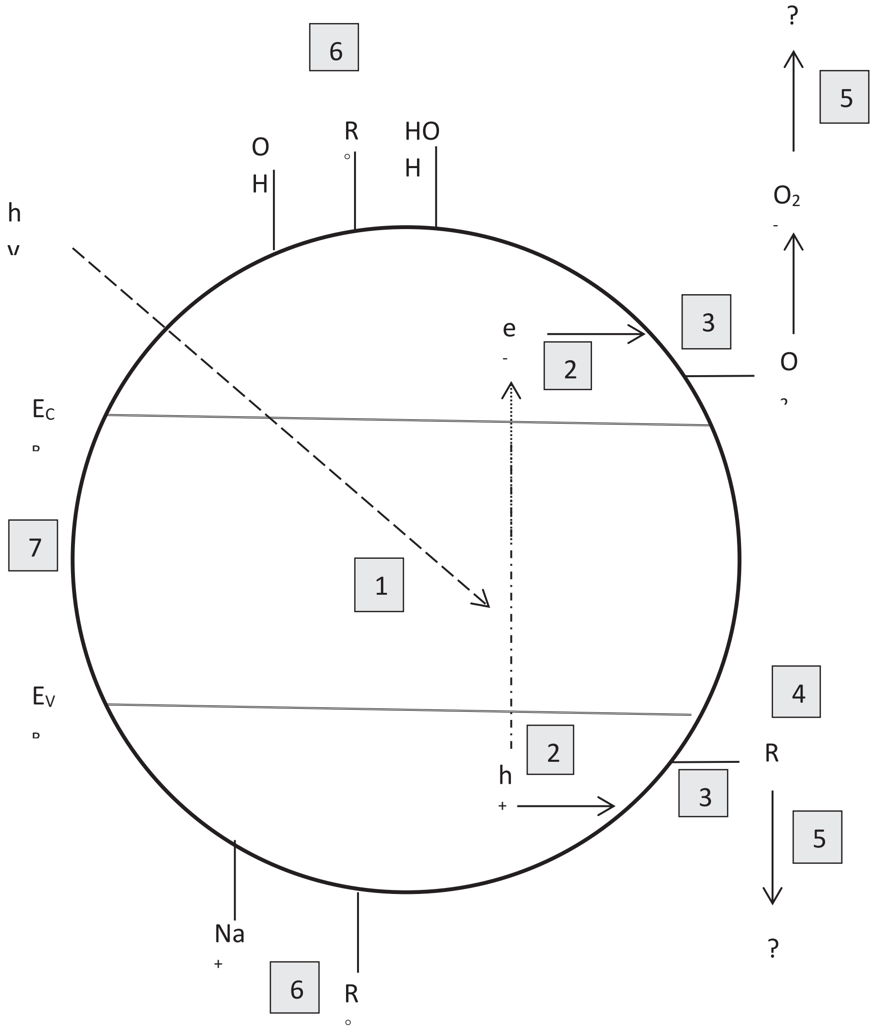

Fig. 8.1 Schematic depicting of the redox steps in the photocatalytic process. (1) Formation of charged carriers (h+ e−) electron–hole pair. (2) Charge transport and trapping. (3) Charge transfer. (4) Chemical adsorption. (5) Redox pathway mechanisms. (6) Scavenger species and reaction promoters. (7) The semiconductor particle surface

contamination, and requires the utilization of little to no nonrenewable resources. Conventional application of the photocatalytic principle requires the activation of the semiconductor photocatalyst using energy in the UV region of the spectrum. The UV sources are predominantly artificial in most research and pilot scale applications, though a fair amount of research by the scientific community is being conducted on the utilization of solar sources (Wang et al. 2018; Pelaez et al. 2012; Chong et al. 2010).

8.5.2.1 Photocatalysis as a Clean Technology

When applied accordingly with the latest technological developments, photocatalysis in its current state qualifies as a clean technology. This is not to be confused with green technology – a working context has been defined for the use of these terms earlier. From a chemical reaction and technological design perspective, the ideal photocatalysts are expected to conform to properties of photoactivity, biological and chemical inertness, stability toward photo-corrosion, suitable for visible or near UV light energy harnessing, be low cost and be nontoxic (Hassan et al. 2016; Aghighi and Haghighat 2015; Ibhadon and Fitzpatrick 2013; Mills and Hunte 1997).

The criterion and feats outlined above have been somewhat achieved through technological developments of titanium dioxide as a most viable semiconductor. The high stability of TiO_2 allows for diverse applications such as in electro-ceramics, glass, and in photocatalytic degradation of chemicals in water and air. The oxide particles can be applied in the form of suspensions in slurry reactors and in the form of thin film coating. The suspended photocatalyst principle has been extensively researched over the years and has been demonstrated to be very efficient degrading different classes of organic compounds. The major concern of the suspended photocatalyst system is the inability to reclaim the semiconductor catalyst in suspended slurry-type applications. This drawback has been addressed in various ways through innovative developments which are specifically aimed at addressing this issue.

In light of the justification above, photocatalysis as a technology does satisfy the criteria as a clean technology in application and is suitable to the degradation of petrochemical pollutants. The only other area of concern with regard to heterogeneous photocatalysis is the energy-intense irradiation in the ultraviolet region of the spectrum required to excite electrons from the semiconductor surface sites to facilitate reduction and oxidation pathways in nonoptimal transparent mediums. This factor is not necessarily a prerequisite for clean technology classification, but would be a requirement for a green technology status classification.

Several studies have investigated the degradation of petroleum waste using heterogeneous photocatalysis and reported success with regard to the removal in the form of COD and TOC (Al-Sabahi et al. 2017; Aljuboury et al. 2015; Tony et al. 2009). Petrochemical organic pollutants are unlike conventional organic chemical contaminants with regard to the treatment reaction protocols used in the degradation process. There is a huge body of scientific knowledge that supports the treatment of organic pollutants using photocatalysis as the successful method of choice. The use of photocatalysis as a clean technology has been demonstrated to be a viable process in the treatment of most organic pollutants.

8.5.2.2 Photocatalysis as a Green Technology

It was alluded that though photocatalysis is in the clean technology bracket, this does not necessarily deem it a green technology, in accordance with the definition context provided. To achieve the green technology status, photocatalysis in application would require the utilization of renewable resources. The major reaction step and element of heterogeneous photocatalysis that has potential in the form of renewable energy is the photo-excitation step. In this step, photon energy is used to create the electron-hole pair that facilitates the oxidation-reduction pathways on the surface of semiconductor photocatalyst. The photon energy required to activate this step falls within the UV region of the light energy spectrum. The UV radiation range of the light spectrum exists at approximately 300 nm (Oppenlander 2003) and has a flux range of 20–30 W/m_2 (De la Cruz et al. 2013).

UV light can naturally be sourced from solar energy, that is, sunlight. Solar radiation constitutes of visible light (43%), infrared light (53%), and UV light (4%). The UV light portion of solar energy can be harnessed and directed toward photocatalytic applications. Various papers have been published on titanium dioxide facilitated oxidation through the application of direct sunlight as the electron energy excitation and promotion step (Blanco-Galvez et al. 2007). Though solar energy is subjected to variations in terms of the geographic latitude, period of the day, cloud cover, atmospheric properties, and seasons (Sirtori et al. 2010), this source of energy qualifies as a green sustainable source.

Advancement of photocatalysis technology toward the utilization of solar energy is the current goal in this sub-discipline. The major obstacle being the amount of energy required to elevate electrons from the valence band edge to the conduction band edge of a semiconductor photocatalyst, such as titanium dioxide. TiO_2, though the most useful and common semiconductor in application, has a relatively large band gap, requiring significant amount of energy in the UV region in order to activate and facilitate the redox reaction schemes. The photon package within the UV domain of solar energy represents a small fraction of this energy requirement, and thus limits the mass transfer efficiency. To fully realize the potential of photocatalysis as a green technology, modifications are required to minimize the energy band gap in order to facilitate visible light absorption. Various scientific literatures have been dedicated to this process with some promising results (Fujishima et al. 2008).

8.6 Challenges in Treatment of Petrochemical Pollutants

The steps involved in petroleum treatment are resource intense. One of the major resource required in the treatment process is water, large amounts of water are used in the refinery process. The principal processes that are responsible for the consumption of most water are hydro-treatment, desalting, distillation, and cooling. In turn, large amount of wastewater effluent are produced from these processes. The wastewater produced from different processes contains constituents indicative to each process and therefore, classified accordingly. In better developed refinery systems, the wastewater from the different petroleum treatment steps is separated and the effluent diverted to different reservoirs. This can allow for treatment of wastewater matrices in accordance to the process of pollutant types. The pollutant loads and the source of the pollutants can determine the level of treatment in the form of the following three treatment step and the preferred methods:

- Primary treatment, the methods that can be applied in this step include buffer tanks, sour water stripper, separators (API/CPI?PPI).
- Secondary treatment, biological treatment and coagulation flocculation-flotation methods are options.
- Tertiary treatment, these include membrane filtration, chemical oxidation, and sand filtration.

Other advantages of such setups are that the loading capacity of wastewater into the treatment plants are reduced thus increasing the efficiency of treatment within unit and allows for a greater variety of reuse options.

Oil and water distribution ratios are another challenge to the treatment of petroleum waste. Treatment of petroleum waste requires insight with regard to the nature of the wastewater in terms of the oil droplet size, distribution, as this has an impact on the efficiency of treatment (Romano 1990). Treatment methods can be configured and adapted in line with the nature of the wastewater from each of the processing units. Several other wastewater chemical treatment methods have been used, such as Fenton process, precipitation, and electrochemical techniques in the treatment of petrochemical waste. These methods have succeeded at producing low quality sludge; the downside of these chemical methods is that they also require large quantities of chemicals, is very costly in terms of operation and maintenance, and requires highly skilled labor (Singh et al. 2016; Hu et al. 2013; El-Naas et al. 2009).

8.7 Conclusion

Photocatalysis as a technology satisfies the criteria of an efficient clean technology, but do not necessarily deem it a green technology without additional developments. As an ideal, photocatalysts are expected to conform to properties of photoactivity, biological, and chemical inertness, stability toward photo-corrosion, suitable for visible or near UV light energy harnessing, be low cost and be nontoxic in nature. The major concern of the suspended photocatalyst system is the inability to reclaim the semiconductor catalyst in suspended slurry-type applications. Several chemical wastewater treatment methods have been used such as Fenton process, precipitation, and electrochemical techniques in treatment of petrochemical pollutants. These methods have succeeded at producing low quality sludge, but the downside of these chemical methods is that these also require large quantities of chemicals, is very costly in terms of operation and maintenance, and highly skilled labors are required.

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Chapter 9
Sustainable Management of Toxic Industrial Effluent of Coal-Based Power Plants

Ramesh Kumar, Alak Kumar Ghosh, and Parimal Pal

Abstract Millions of tons of coke are produced to meet the demand of manufacturing of iron and steel industry and coal-based power plants with rapid urbanization. The conversion of coal to coke is one of the major sources of environmental pollution, because this process generates huge volume of coke-oven wastewater (COWW) during quenching of hot coke. The discharged wastewater contains cyanide, thiocyanide, ammonium-N, phenols with high biological oxygen demand, chemical oxygen demand, total dissolved solids, total suspended solid, and polyaromatic compounds pose a threat to the existing flora and fauna of the ecosystem. In this chapter, detailed information is provided about the generation, characteristics, toxicity and harmful effect on environment of COWW. In addition, different sustainable technologies such as biological, physical, and integrated processes have been proposed for the sustainable treatment of COWW while comparing their merits and demerits with those of the existing technologies.

Keywords Coke-oven wastewater · Biological treatment · Physical treatment · Membrane separation · Adsorption · Struvite recovery

9.1 Introduction

The conversion of coal to metallurgical coke finds application in blast furnace of steel plant and coal-based power generation across the world. In addition, coke is also used in the foundries and domestic purposes. However, during coke conversion, gases and other by-products such as benzene, toluene, anthracene, naphthalene, and

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coal tar are produced, which are the raw materials for various dyes and explosives (Chu et al. 2012). Approximately, 4000 m^3 of fresh water is consumed for the washing and cooling of hot coke mass, coke-oven gases, NH_3-N still and by-products of coke industry for the production of 100 ton of metallurgical coke which eventually generates 100 m^3 of wastewater (Pal and Kumar 2014). Highly hazardous and toxic pollutants such as phenols, cyanide, thiocyanide, NH_3-N, polyaromatic hydrocarbons (PAHs), oil, and grease are present in the wastewater which could contaminate surface water, groundwater, and low-lying areas. Their concentrations depend on the types of coal and the operating conditions in the coke industry (Burmistrz and Burmistrz 2013).

Biological methods have been used for long time for the treatment of organic pollutants present in the industrial wastewater at a relatively low cost. Due to the slow process, biological treatment is normally required for the long residence time of the biodegradation pollutants present in the coking wastewater (Lu et al. 2012; Bharagava et al. 2014; Kishor et al. 2019). Toxic pollutants like cyanide, phenol and high concentration of ammonium-N are normally not favored for the growth of autotrophic and heterotrophic oxidizing bacteria during oxidizing of ammonia (Ma et al. 2016).

Different chemicals such as alum, iron, and polymers are used during pretreatment of wastewater for coagulation and settlement of suspended particles to minimize the adverse effect of biodegradation. Presence of cyanide is the most toxic compound in COWW for which different methods have been tried like INGO process (International Nickel Company Limited) in which SO_2/air is used, Caro's acid method, alkaline chlorination, ozonation, acidification-volatilization and re-neutralization process, electrolytic oxidation, Fenton's treatment, photocatalytic, ion exchange, and catalytic oxidation processes. However, there are limitations in each methods, e.g., during alkaline chlorination, some more toxic compounds may be generated such as cyanogen chloride. For the removal of phenolic compounds, adsorption, oxidation (chemical or enzymatic), solvent extraction and biodegradation have been investigated in the literature (Lai et al. 2007; Bharagava et al. 2008a, b; Pal and Kumar 2014). Recently, membrane-based technology is used as an alternative to biological treatment of COWW to concentrate the pollutants and reduce the volume of wastewater. Few researchers have investigated the use of traditional reverse osmosis (RO) membrane for the separation study of major pollutants from the wastewater like cyanide, phenol and ammonium-N.

However, use of RO membrane has limitations such as requirement of high transmembrane pressure, low flux, high membrane cost, frequent membrane fouling and regular maintenance of the system. Nanofiltration (NF) membrane is an emerging technology which can be exploited for the separation of small ions or impurities from waste effluents at a relatively low operating pressure with better flux than RO membranes.

Wastewater may be used as resource and reused for irrigation or recycled in the same industry through proper treatment and sustainable management. A paradigm shift is required in wastewater management in the back drop of gradual decrease in per capita availability of fresh water, increasing population, rapid industrialization and urbanization (Pal and Kumar 2014). Thus, in this chapter, we have tried to find out the new approaches toward developing sustainable treatment technology by incorporating the concept of recycling, resource recovery and reuse. The economic viability of wastewater treatment plant may be enhanced by recovery of value added products.

9.1.1 Generation and Composition of Coke Wastewater

Conversion of coal to metallurgical coke by anaerobic carbonization, a large volume of gas and wastewater are generated from which economically valuable by-products could be extracted. The recovery of by-products and generation of wastewater during operation of coke industry has been shown in the flowchart in Fig. 9.1. The chemicals extracted from the coal have the good selling value. A typical operation of large coking plant is shown in Fig. 9.2, which depicts the conventional way of conversion of coal to coke with inflow of coal, lime, nitric acid and outflow of coke and other by-products such as tar, benzene, fertilizer. A huge quantity of wastewater is generated during the washing of coke gas such as ammonia, phenol, cyanide, thiocyanide, sulfide, tar, oil and grease. The general characteristics of coking wastewater have been given the Table 9.1. Fine suspended particles float on the surface, whereas heavy suspended particles are settled at the bottom. COWW is highly complex, yellowish color and ammoniacal in odor as the effluents are generated due to washing of ammonia stills. If such wastewater is disposed to any water body, then marine life can be affected seriously due to suspended particles choking the respiratory organs of fish. Generally, 1.6 m^3 of wastewater is generated for making 0.6 g of coke.

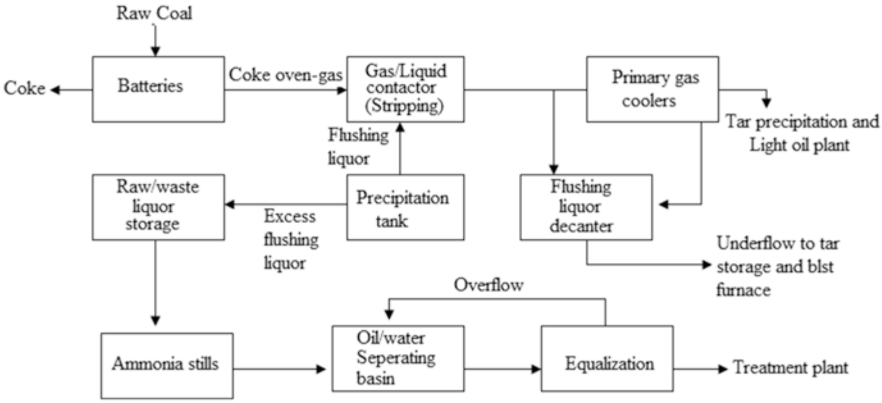

Fig. 9.1 Simplified flow-sheet for coking wastewater generation. (Reprinted from Pal and Kumar (2014) with permission of Taylor and Francis)

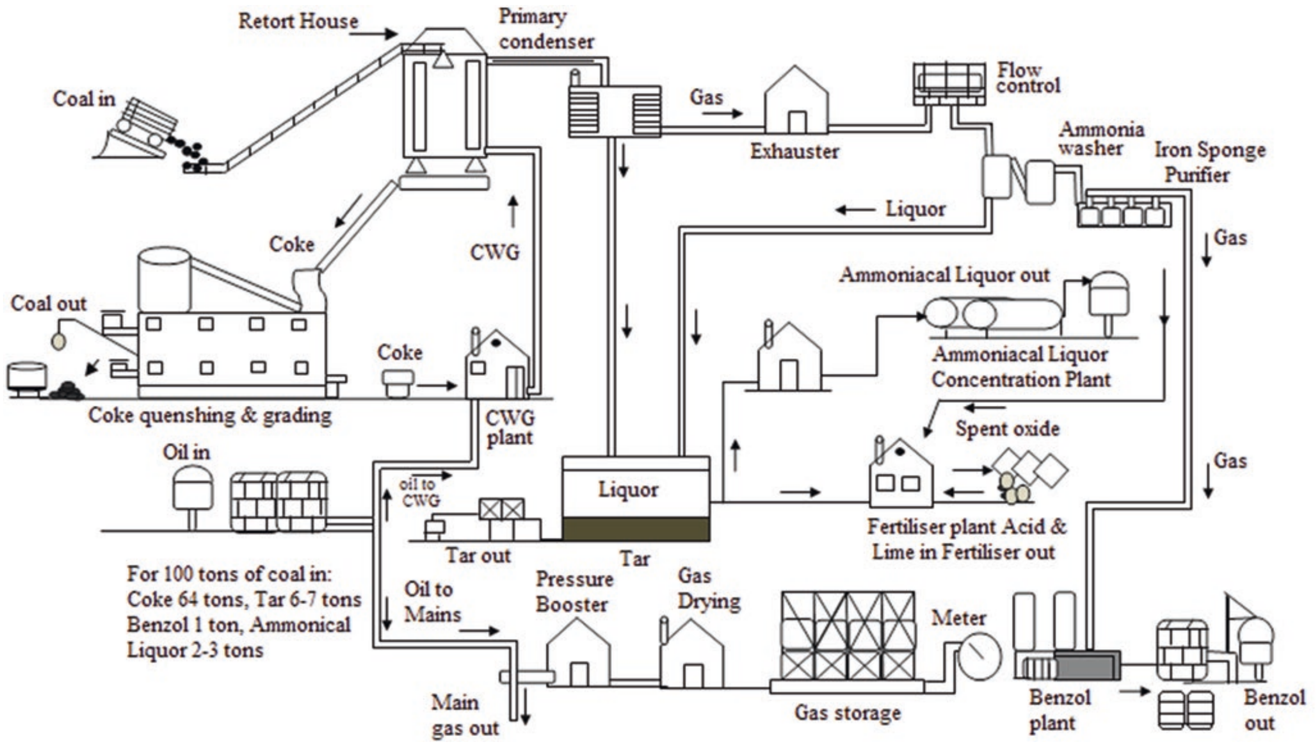

Fig. 9.2 Typical scheme of conversion of coal to coke while recovery of by-products and generation of ammonium-N wastewater. (Reprinted from Pal and Kumar (2014) with permission of Taylor and Francis)

Table 9.1 Typical composition of raw coking wastewater

Major parameters	Concentration range (mg/L)	Tolerance limit (mg/L) (IS 2490 part VIII, 1986)
COD	2100–3000	50
Ammonium-N	2550–3500	250
Phenols	155–225	0.5
Cyanide	25–75	0.2
Thiocyanate	155–185	–
Total dissolved solids	12,500–13,400	–
Oil and grease	42–55	<10
Salinity	6–8	–
Fluoride	70–85	<1.5
Chloride	540–570	<1000
Sodium	245–265	<60
Sulfate	32–39	–
Phosphate	50–73	–
Magnesium	30–36	–
Bicarbonate	1500–2100	
pH	9.0–9.7	6.5–9.0

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9.1.2 *Sampling of Wastewater*

Grab sampling is one of the methods for sample collection, and quick analysis should be preferred. However, separate samples are collected and stabilized by different mode, depending upon the pollutants presence. For example, phenols present in wastewater are subjected to chemical and biological oxidation. Thus, such sample should be preserved and stored properly. Similar samples may be acidified to pH of 4 by H_3PO_4. Copper sulfate is added in 1 g/L to inhibit the biodegradation and stored in refrigerator at 4 °C for the analysis of biological oxygen demand (BOD). However, for COD analysis, the sample must be acidified with H_2SO_4 by 2 mL/L. All parameters of the wastewater must be analyzed as per “Standard Methods” for the examination of wastewater given in APHA (2012).

9.1.3 *Toxic Nature of Wastewater*

The environmental impact by coking wastewater has become a very serious issue due to its complexity, heterogeneity, and toxicity, and it highly depends upon the extent of treatment before the discharge. The effluent contains xenobiotics, phenols, and some derivatives (such as pyrogallol, quinone, and pyrocatechol) in addition to cyanide, ammonia, and thiocyanide. The total cyanide and phenols may be high up to 80 and 1200 mg/L. Thus, coke wastewater is very toxic and it may lead to sudden failure of biological treatment plant. Therefore, it is necessary to comprehensively study the residual contaminants present in the treated effluent using chemical and bioassay analysis to ensure the environmental safety. The effect of bio-toxicity by the industrial effluents is dependent upon the species, concentration, presence of toxic compounds, and solubility of compound in receiving water (Tian et al. 2012; Pollice et al. 2008; Bharagava et al. 2008a, b; Escher et al. 2013).

The value of toxicity is measured by E(L)C_{50} (EC_{50}-mea or LC_{50}-mea) which is the ratio of total concentration of detected chemicals as the product of E(L)C_{50} value from the test to the total concentration of the target compounds. The toxic effect had been investigated by few researchers in plants like *Zea mays*, *Vicia faba,* and *Hordeum vulgare* by considering various parameters including growth, fresh biomass, mitotic index, micronucleus frequency and antioxidant capacity (Dong and Zhang 2010). Bioassays and chemical analysis were done in *Vibrio fischeri* and *Daphnia magna* while growing in effluent of a semi-coking wastewater treatment plant to evaluate the bio-toxicity. The treatment by coagulation and adsorption followed by anaerobic and oxic-biological treatment showed successful achievement of more than 90% removal of pollutants with 90%, 94.8% and 81% of benzene, phenols and PAHs, respectively.

However, the final effluents still had the bioluminescence inhibition toxicity toward *V. fischeri* whereas lethal toxicity to *D. magna*. To reduce the ecological risk and to protect the aquatic environment from the COWW, some alternative promising technology such as membrane bioreactor was suggested as an efficient technology (Ma et al. 2017). Another researcher had claimed that the adsorption treatment followed by the physiochemical and bio-chemical combined treatment was found suitable for the final discharge of the effluent as confirmed by the genotoxicity evaluation in *V. faba* (Liu et al. 2017). Furthermore, the anaerobic and aerobic biodegradation was suitable for the removal of benzene, indoles and quinolones, but for PAHs removal, advanced treatment was required such as adsorption.

9.2 Conventional Treatment Methods

9.2.1 Physiochemical Methods

Physiochemical methods are used for the removal of colors, colloidal, suspended, floating particles and toxic compounds by using different methods like oxidation, precipitation, adsorption, ozonation, advanced oxidation process, electrolysis and membrane-based system (Parga et al. 2003; Barakat et al. 2004; Barriga-Ordonez et al. 2006; Park et al. 2008a, b). The novel coagulant as polyferric sulfate had been used as neutral or cationic polymers for removal of total cyanide present in the coking wastewater (Shen et al. 2014). Settling tanks are used to settle down the suspended solids to facilitate the biological treatment of coke wastewater successful. Addition of lime slurry in secondary sedimentation tank and use of synthetic zeolite are very useful for the physiochemical treatment and ammonia removal, respectively.

For the removal of hazardous compounds, adsorption process was used to remove the contaminants up to 90–95%. However, continuous mode of treatment and frequent replacement and regeneration are the major limitations of the adsorption process. Ammonia removal was done using steam stripping, however, high pH (>7.0) value is required for this process. In addition, through this process, pollutant (ammonia) is being shifted from water to air (El Diwani et al. 2007). This process needs huge capital investment for purchasing the equipment, such as stripping tower, pump, liquid spray system, forced air and carbonization system. Fouling problems, sludge production and release of ammonia gas in to air are the other drawbacks of steam stripping. This system is very useful for capturing and conversion of ammonia into useful products as shown in Fig. 9.3. To remove the organic contamination, wet air oxidation has been used to bring down the chemical oxygen demand (COD) values of wastewater. Salt precipitation is the major challenge of such type of process (Kumar and Pal 2015a, b).

For the removal of toxic and hazardous pollutants from the wastewater, ultrasonic energy has been used to form the acoustic cavitation. The effect on pollutants during ultrasonic irradiation may vary on initial pollutants concentration, saturating gas and density of irradiation. However, high power density of ultrasonic waves and initial low COD concentration appropriates for the better degradation of pollutants (Mason 1990; Okouchi et al. 1992; Ning et al. 2005). During ultrasonic irradiation treatment, transient state forms at high pressure and temperature and yields CO_2 and H_2O and hydroxyl radical of the pollutants. Sometimes metallic catalysts are used to enhance the reaction rate.

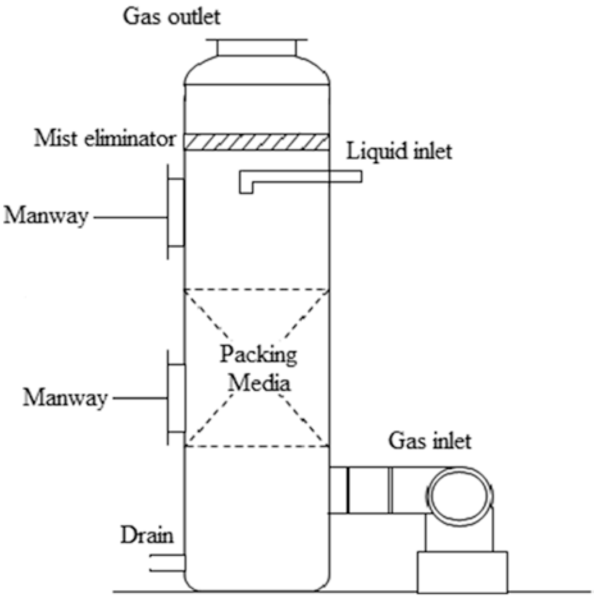


Fig. 9.3 Typical steam stripping for ammonia gas

9.2.2 Biological Treatment

9.2.2.1 Single-Step Activated Sludge Process

The most economical and viable option is the activated sludge process (ASP) for the treatment of such a huge quantity of wastewater. In the ASP process, a dense microbial population at their exponential growth phase in suspension is used to decompose and degrade the organic pollutants (Zhang et al. 2010a, b). A simplified scheme of single stage activated sludge process with aeration and sedimentation tank has been shown in (Fig. 9.4). Microbial growth rate is high in the presence of unlimited food and oxygen in the reactor in addition to the provision of recycling of sludge further by helping to maintain the microbial population and degradation of the organic compounds. Activated sludge is developed in a reactor attached to the sedimentation tank for the treatment of the coke oven wastewater where dense microbial flocks are adsorbed and assimilate the organic matters and mineralized by complete oxidation and generate new microbial cells. Different pollutants like COD, phenols, cyanide, thiocyanates, ammonium-N were reduced to 75, 98, 90 and 71%, respectively, achieved during single-step activated sludge treatment (Vázquez et al. 2006a, b). However, due to presence of a number of pollutants and fluctuation of concentration and presence of some toxic compounds like cyanide, thiocyanates, phenols often lead to failure of biological system. These limitations of single-step ASP have been overcome by the several modifications and addition of some steps.

9.2.2.2 Multistep Activated Sludge Process

Complex and multi-pollutants coking wastewater needs multistep processes involving different microorganisms with different environmental conditions like aerobic, anaerobic and anoxic. Ammonia gets converted into nitrite and nitrate by autotrophic

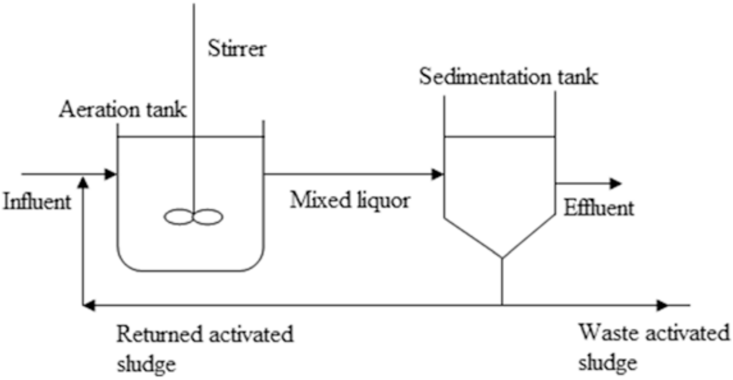


Fig. 9.4 A typical scheme for activated sludge process (suspended). (Reprinted from Pal and Kumar (2014) with permission of Taylor and Francis)

nitrifiers in aerobic conditions, whereas thiocyanate gets converted into ammonia and sulfate by autotrophic oxidizing conditions at low pH (Zhang et al. 2010a, b). The nitrite and nitrate present after aerobic treatment of ammonium-N by *Nitrosomonas* and *Nitrobacter*, heterotrophic denitrifiers convert to nitrogen gas using organic pollutants like phenols as a nutrients at high pH. It acts as an electron donor for the denitrification reaction (Richards and Shieh 1989). Two step ASPs had been investigated for the biodegradation of coking wastewater at two different hydraulic residence time (HRT) of 98 and 86 h for first and second reactors with removal efficiency of 91, 99, 98, 99% of COD, phenols, thiocyanates and ammonium-N, respectively, at operating temperature of 35 °C.

Pollutants-based HRT and recycling ratios help to overcome the inhibition phenomena of high concentration of the pollutants though the speed of degradation may decrease. Sometimes methanol is added as a carbon source for the denitrification at the end of the process in anaerobic condition; however, to bring down the cost, denitrification process may be placed at the head of the process to utilize the existing organic pollutants as carbon source (Chakraborty and Veeramani 2006). Removal of cyanide still remains a big challenge in the final effluent due to very slow biodegradation in aerobic and anaerobic reactors. In addition, the concentration of cyanide is the major limiting factor for the extent of removal of other pollutants present in the coking wastewater (Dash et al. 2008). A schematic diagram of a typical multistep ASP is shown in (Fig. 9.5).

9.2.2.3 Activated Sludge in Sequential Batch Reactor

In sequential batch reactor (SBR), the aeration, treatment and sludge settlement are done in the same tank. It operates in non-steady state, in batch mode. The reaction pathway and the kinetics of biodegradation of thiocyanates was evaluated using oxygen evaluation rate and sulfur and nitrogen balance data during the activated sludge treatment in two SBR units (Staib and Lant 2007). The treatment of coking wastewater was also studied in a pilot plant consisting SBR in addition to the stripping unit and homogenizer unit. The system had the removal efficiency of 69%,

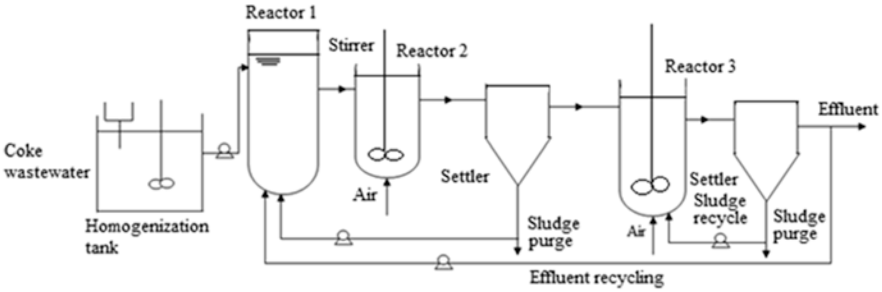


Fig. 9.5 A typical schematic diagram of multistep ASP. (Reprinted from Maranon et al. (2008b) with permission of Springer)

98% and 90% of COD, phenols and thiocyanate, respectively, at 58 h of HRT (Maranon et al. 2008a). However, the maintenance of such large system with sophisticated controls, automated switches, valves and requirement of post-SBR treatment are complex and expensive.

9.2.2.4 Fixed Biofilm-Based Treatment

The microbial system grows and forms a film-type structure on the inert and solid medium (carrier) which provides large surface area. The carriers are of ring- and/or string-type structure and made up of soft or semisoft materials. Cube structured foam made up of polyurethane with micro and macro pores could be the better choice for growing and trapping the microbes due to high porosity and water content. Such low density materials of polyethene was used for growing microbes in a moving bed bioreactor with filling ratio of 50% and suspended by air flow from the bottom of the reactor that could remove 91 and 96.8% of COD and ammonium-N (Li et al. 2011). Treatment of coking wastewater is done during the contact of microbial film with pollutants in the reactor without the need for recirculation of biomass as most of them retain within the reactor.

The environmental condition of growing bacteria may be aerobic, anaerobic, and anoxic depending upon the thickness of biofilm as the oxygen can diffuse to certain level. The removal of ammonium-N and COD were 98.9 and 92.4%, respectively, achieved by coking wastewater using the multistep fixed biofilm system of anaerobic-anoxic-oxic at low HRT of 31.6 h (Zhang et al. 1998). This system has proved to be better than free cells based activated sludge system for the degradation of pollutants during shock and fluctuating loading of wastewater. A typical scheme of anaerobic, anoxic, and oxic reactor with fixed biofilm-based system for coking wastewater treatment scheme has been shown in (Fig. 9.6).

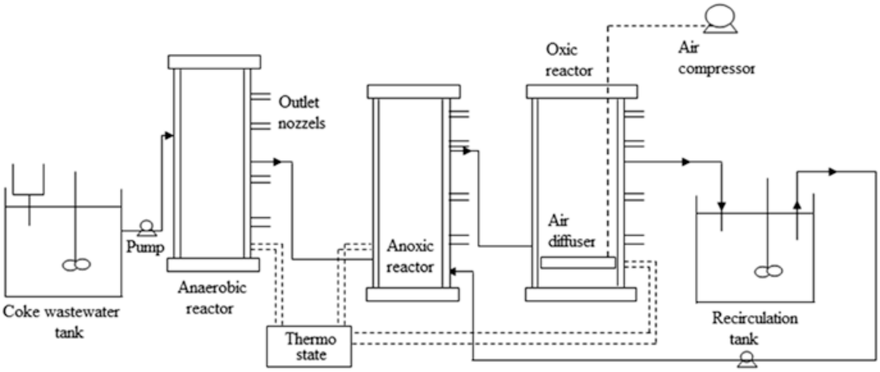


Fig. 9.6 A typical anaerobic-anoxic-oxic fixed biofilm based plant. (Reprinted from Zhang et al. (1998) with permission of Elsevier)

9.2.2.5 Biological Aerated Filters-Based Treatment

In case of biological aerated filters (BAF), the support medium remained submerged completely in wastewater and active biofilm grows on the surface of that support medium (Fig. 9.7). At the base of the reactor, the oxygen is supplied through a diffuser in upward direction to create a suspension phase of support medium. The thickness of biofilm is better due to availability of high surface area of media to the microbial films which can efficiently degrade and utilize the organic pollutants. Sometime biological-activated carbon (BAC) acts as the support medium for the growth of biofilm. BAC in combination with Fenton's reagent was used for the successful and cost-effective treatment coking wastewater up to recycling stage (Jiang et al. 2011). The final treated effluent from Fenton oxidation–BAC treatment was better in quality as the BAC function was adsorbent.

9.2.2.6 Fluidized-Bed Reactor-Based Treatment

In aerated fluidized-bed reactor (AFBR), small and lightweight support materials with high surface area are used, such as sand, glass or anthracite (size <2 mm) for the growth of biofilms in suspended mode. AFBR could provide considerable amount of biomass as high as 40,000 mg/L for the better, quick, and cost-effective removal of organic pollutants present in the coking wastewater (Marvan et al. 1992). In AFBR, the wastewater is moved from bottom to upward direction and passes through the bed of biofilm containing activated carbon (granular shape) or sand in the rectangular shape of the reactor at the speed to expend and create the suspension state. These media particle in the reactor provide vast surface area for the growth of the biological film resulting in five to ten times higher biomass concentration than the conventional bioreactor (Fig. 9.8). AFBRs are highly compact systems, but operation cost is high due to need of high pumping pressure and pure oxygen for the growth of the microorganisms.

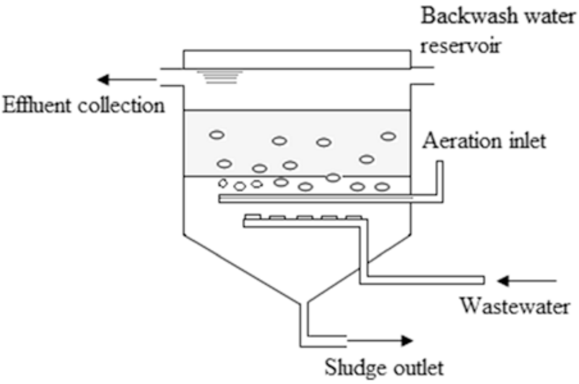
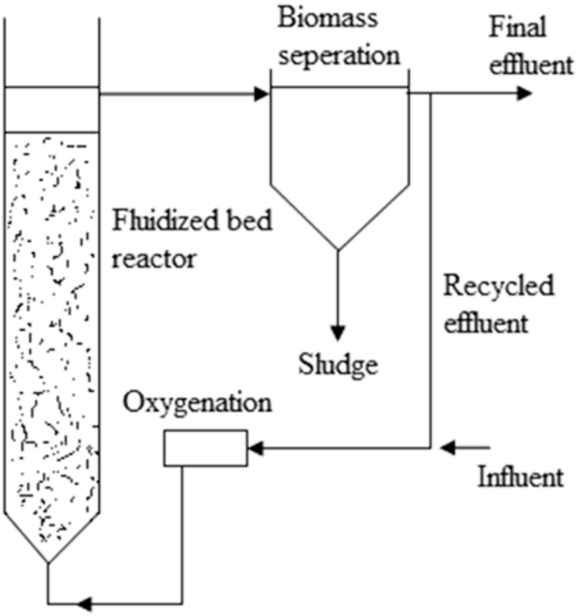


Fig. 9.7 Submerged type of biological aerated filter. (Reprinted from Pal and Kumar (2014) with permission of Taylor and Francis)

Fig. 9.8 A typical design of fluidized-bed reactor. (Reprinted from Pal and Kumar (2014) with permission of Taylor and Francis)



9.2.2.7 Bioaugmentation-Based Treatment

Treatment of coking wastewater with activated sludge made up of specialized microorganism of targeted pollutant is known as bioaugmentation. It is a better technology with improved flocculation and settling of activated sludge during the treatment of the wastewater. Specialized bacteria like *Burkholderia picketti* had been used in the anaerobic-anoxic-oxic environment for the bioaugmentation-based treatment (Jianlong et al. 2002). At different environmental conditions like anaerobic, anoxic and oxic, different commercial microorganisms were used for the pollutant-specific bioaugmentation of coking wastewater. The metal complex cyanide was treated with specialized laboratory-grown microorganism yeast (*Cryptococcus humicolus*) in fluidized-bed reactor by applying the bioaugmentation principle (Park et al. 2008a, b). Bioaugmentation process is very useful for the treatment of toxic and recalcitrant pollutants.

In addition to upgrading and seeding of wastewater treatment plants, these commercially grown microbes are very useful for maintaining the suitable environmental conditions for the degradation of pollutants during wastewater treatment. These microbes must be resistant to the environmental stress conditions like high temperature, sunlight and predation by natural microbes. However, poor adaptability and high cost are the major limitation of commercialization of bioaugmentation-based wastewater treatment.

9.3 Integrated Treatment Approach

9.3.1 Membrane Bioreactor Followed by Biological Treatment

Due to ever increasing demand for quality of treated effluent and satisfying minimal permissible limit of pollutants fixed by pollution control boards, integrated treatment technology gains importance. In view of scarcity of fresh water and necessity of reclamation of water from wastewater, a complete treatment technology is required which should not only remove the chemical pollutants but also eliminate the viruses and bacteria present in the wastewater (Lubello et al. 2007). This can be only possible through use of membrane bioreactor (MBR) or final polishing treatment of effluent of biologically treated effluent by membrane-based system. Submerged membrane bioreactors are very useful for wastewater treatment to generate sludge-free effluent (Liu et al. 2005; Marrot et al. 2004).

Moreover, ultra and microfiltration membrane of different pore sizes, which varies from 0.13 to 0.45 μm, not only retain the bacteria but also viruses (Yang et al. 2006). High density of microorganism could be possible by the complete retention of microbes using membrane system. This creates the situation of low food to biomass ratio and utilizes maximum part of the organic and inorganic pollutants present in the wastewater for only maintenance of biomass and less for growth. To comply with the stringent environment regulation and frequent fluctuation and high loading rate of influent raw wastewater, the MBR is observed as the most efficient process for the treatment of industrial as well as municipal wastewaters (Glen et al. 2005; Qin et al. 2007). The MBRs are more advantageous than conventional ASP as better quality of effluent could be found from the former even at high and fluctuating loading rate and reclaimable water can be extracted by subsequent reverse osmosis/nanofiltration-based membrane separation (Reemtsma et al. 2002).

A bench-scale comparative study was performed for the treatment of coking wastewater using anaerobic, anoxic and oxic reactor with submerged MBR and conventional ASP system for the long-term removal of organic and inorganic pollutants with total retention of sludge. It was found that the system attached to MBR was more reliable and efficient in pollutants removal of 88, 100 and 100% of COD, turbidity and ammonium-N, respectively (Zhao et al. 2009a, b). However, membrane fouling during operation by colloidal fraction of carbohydrates and proteins is the major constraint for industrial applicability MBR results in deterioration flux during the dead-end filtration module (Zhao et al. 2010). Substantial reduction in the fouling could be achieved using cross-flow MBR (Rahman and Al-Malack 2006).

9.3.2 ASP Integrated with Chemical Pre-treatment

High ratio of circulation (300–400%) is required to dilute the toxic effect of cyanide and ammonium-N during the biological treatment of coking wastewater. However, this would delay the treatment of huge industrial effluent and result in high treatment cost (Vázquez et al. 2006a, b). Thus, chemical pre-treatment is the suitable option to decrease the toxic pollutants concentration and thus decrease the dilution of wastewater by recirculation. Application of Fenton's reagents and coagulation-flocculation may be applied during pre- and/or post-treatment of coking waste water to facilitate the biological treatment and get a better final treated effluent. Different chemical compounds like iron salt, alum and iron powder are good coagulants used for the solid–liquid separation before the biological treatment (Ghose and Kumar 1993). Zero valent iron can reduce and transform the structure and minimize the toxic effect of the pollutants. Organic, inorganic and polyaromatic compounds are mineralized using Fenton's oxidation. Major hazardous compounds like cyanide and phenols are degraded using Fenton's treatment.

In addition, high concentration of ammonium-N was precipitated to struvite by using equimolar molar concentration of magnesium and phosphate salts. Struvite could be used as a slow-releasing fertilizer (Kumar and Pal 2015a, b). Sometimes extraction replacement–biodegradation integrated approach was used to reduce the COD up to 88.63% from the wastewater. Extract such as *n*-octane and cyclohexane were used to remove the heterocyclic compounds like pyridines and quinolones to facilitate the biodegradation (Yuan et al. 2012). A comparative study about the advantages and limitations of the different methods has been shown in Table 9.2.

9.4 Extraction Value Added Products from the Coking Wastewater

To extract the nutrients like ammonium-N and phosphate from the nutrients-rich wastewater, chemical precipitation method is applied to form magnesium ammonium phosphate (MAP), popularly known as struvite. Nutrient-rich wastewater point sources varies from municipal, landfill leachates, anaerobic digested sewage sludge to some industrial wastewater such as coal-based power plants, dairy plants, leather, textile and paper-pulp effluents (Bharagava et al. 2009; Chandra et al. 2011; Kishor et al. 2019; Zainith et al. 2019). In controlling the high concentration of nutrients present in the wastewater, it may deteriorate the quality of receiving water. Now, the focus has gradually shifted from removal to recovery with emphasis on the sustainability and maintaining the water quality to alleviate the environmental pressure (Uysal et al. 2014).

If such wastewaters are discharged without treatment, then nutrients load in the receiving fresh water will increase and cause eutrophication which promotes excessive growth of algae and plankton (de-Bashan and Bashan, 2004). These destroy the aquatic diversity by producing toxic algae and also lead to soil acidification due to the leaching effect. Thus, extraction of nutrients in the form of struvite by balancing molar ratio of magnesium, ammonium and phosphate helps to stop the eutrophication. Struvite or MAP is a white crystalline powder, sometimes deposited on the pipelines during anaerobic digestion due to presence of high and equimolar

Table 9.2 Comparative study of different treatment approaches/technologies of coke oven wastewater with advantages and limitations

Treatment technology	Advantages	Limitations	References
A. Physicochemical methods			
Sedimentation/ floatation	Settling tanks are used to recover the coke particles, oil, and greases; addition of lime slurry facilitates sedimentation; NH_3-N removed by zeolite column	Failures of sedimentation result in loss of coke breeze and create problem during biological treatment	Ghose and Kumar (1993)
Adsorption	Mostly used activated carbon; 90–95% removal of contaminants	Mostly carried out in batch mode; need of frequent replacement/regeneration of adsorption bed material	Moussavi and Khosravi (2010)
Steam stripping	Use for the removal and recovery ammonia as a by-product	pH lower than 7 is required; significant capital investment; shifting the ammonia from wastewater to air	Marr and Koucar (1993)
Wet air oxidation	Useful for high COD removal	Salt precipitation and plugging in the reactor Ammonium-N destruction is difficult	Marrone et al. (2004)
Chemical oxidation	Use of Fenton's reagents to degrade the persistent organic pollutants and cyanide	Low pH adjustment and chemical sludge generation make the process unattractive	Jiang et al. (2011)
Coagulation and precipitation	Useful for the removal of organic halides, total organic carbon, color and ammonium-N Precipitation by zero-valent iron, Mn, and Mg	Sludge generation is the major problem	Lai et al. (2007)
Ozonation	Useful for the removal of COD, TOC, color, CN^-, SCN^- and phenols; Ozone generator and KI solution are required	Complex process and operation make the process unattractive	Chang et al. (2008)
Electrochemical oxidation	Useful for the treatment of bio-refractory and toxic compounds; however, depend upon materials Used for making anode	High energy consumption for electrochemical oxidation makes the process economically not feasible	Zhu et al. (2009)
Membrane technology	Suitable for volume reduction and reclamation of reusable water using different membrane such as MF, UF, NF and RO membranes	Fouling and high cost of membrane are the major limitations	Kumar et al. (2011)

(continued)

Table 9.2 (continued)

Treatment technology	Advantages	Limitations	References
B. Biological methods			
Suspended growth process: single step	A floc of actively growing bacteria in suspension known as activated sludge use to degrade organic pollutants; low cost process; Suitable for municipal wastewater treatment	Toxic pollutants such as cyanide and loading variation concentration lead to failure of biological treatment; external carbon source require to grow the microbes; high HRT makes the process too slow	Vázquez et al. (2006a)
Multistep ASP processes	Pollutant-specific environmental condition such as aerobic, anoxic, and anaerobic are provided to	Difficult in maintenance; external carbon source such as methanol is required;	Maranon et al. (2008b)
	Degrade the different pollutants; More than 90% degradation of pollutants at HRT of 80–90 h	Bigger area is required	
Sequential batch reactor with ASP	Provide dynamic data; kinetics and rates of removal of pollutants with activated sludge; better removal for phenols in low HRT (58 h)	Presence of cyanide inhibit the degradation specially thiocyanate; high level of sophistication is required	Staib and Lant (2007)
Fixed biofilm system	Biofilm grows on inert, soft, semisoft medium called carrier; It may be multistep; better degradation efficiency	Long start-up time for the biofilm formation; overgrowth of biofilm leads to elutriation of carrier; high pressure air flow from to bottom	Yang et al. (2006)
Biological aerated filters (BAF)	Biofilm grows on the support medium completely submerged in the wastewater	Long time of acclimatization is required	Vázquez et al. (2006b)
	Integrated with biological activated carbon	High surface area of activated carbon is needed	
		High pressure pump is required for aeration	
Aerobic fluidized-bed (AFB) reactor	Biomass developed in small media (0.2–2 mm) made up of glass and anthracite provide large surface area; generate high biomass concentration 40 g/L; highly compact system	Expensive to run due to the cost of pure oxygen; high pressure pump is required	Marvan et al. (1992)

(continued)

Table 9.2 (continued)

Treatment technology	Advantages	Limitations	References
Bioaugmentation	Use of pollutant-specific microbes; commercial microbes successfully degrade complex pollutant; need low HRT to degrade toxic and recalcitrant pollutants	Required suitable conditions and expensive culture; problem in adaptability	Park et al. (2008b)
C. Hybrid treatment process			
Biological treatment integrated with membrane bioreactor	System resistant to high loading rate and fluctuation in concentration; improved treatment efficiency with refractory organic pollutants; polish the effluent quality for possible reuse by NF/RO	Fouling of MBR; difficult in running for long hours	Zhao et al. (2010)
Combined methods of ultrasonic radiation; catalytic oxidation and ASP	Useful for removal of toxic and hazardous pollutants; degrade into CO_2 and H_2O; Low HRT required	Expensive process; high temperature and pressure are required; high maintenance is	Ning et al. (2005)
Biological process combined with chemical pre-treatment biological treatment	Chemical pre-treatment helps to remove toxic pollutants and facilitate biological treatment; avoid the recirculation; coagulation use to separate solid suspended from liquid	Chemical sludge generation is a major problem; costly extractant such as octane and cyclohexane is required to remove pyridines and quinolones to facilitate	Yuan et al. (2012)

concentration of Mg^{2+}, NH_4^+-N and PO_4^{3-} in the wastewater (Ren et al. 2010). Civil engineers and chemist have tried theoretically and experimentally to recover struvite (Hao and van Loosdrecht 2006; Ronteltap et al. 2007). Struvite has been used as a slow-releasing fertilizer; 1 kg of struvite can fertilize 2.6 ha of arable land.

The application of struvite in agriculture land could reduce the need of rock phosphate and stimulate the growth of vegetables by releasing the P and Mg without any heavy metal contamination. Thus, as a fertilizer, it has commercial value and it is being sold in Japan by fertilizer companies (Ueno and Fujii 2001). Such types of fertilizer would be very effective in comparison to conventional soluble fertilizers in grassland and forest wherein fertilizers are used once in several years. Struvite has also been used for ornamental plants and appropriate for use as turf in tree seedling, vegetables, and flowers. Other useful compounds like ammonium thiosulfate, ammonium thiocyanate, and sometime energy in the form of methane gas during anaerobic digestion of phenols have also been recovered (Perez et al. 2002).

9.5 Membrane Separation Technology for the Treatment of Coking Wastewater

Recently, membrane-based separation is being considered to be one of the most important, efficient, and useful separation technologies in the chemical and allied process industries and successfully can compete with conventional separation processes. Membrane is the barrier, placed between two mediums that allow one or more components selectively by applying some external pressure. The membrane separation may be of cross-flow type where the feed travel parallel to the membrane surface and one or more components diffuse or pass through the membrane as shown in (Fig. 9.9). Membrane may be porous or nonporous and divided into three category, viz. polymeric, liquid membrane, and inorganic membrane.

Further based upon the transport process, pore size, and membrane characteristics, membrane process can be categorized as follows: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The NF membranes are in between of UF and RO membranes (Kumar and Pal 2015a, b). The major advantages associated with the NF membrane are as follows: low operating pressure; high flux; high retention of multivalent ions, salts and organic matters; separation can be carried out at mild conditions of pH and temperature; consumes less energy as it does not involve any phase change except evaporation; relatively low investment, maintenance and simple mechanical operation; high selectivity; continuous operation may be possible.

NF membrane separates the solute based on size exclusion mechanism and (steric or sieving) and Donnan (electrostatic) mechanisms (Strathmann et al. 1992). The rejection study of different pollutants present in the coking wastewater had been investigated by four types of NF membranes. The effect of pH, cross-flow rate (CFR), transmembrane pressure (TMP) and recovery ratio have been optimized (Kumar et al. 2011; Kumar and Pal 2013). The experimental set-up was made up of stainless steel (SS-316) which consisted two cross-flow membrane modules for MF and NF membranes, two stirred SS tank and a peristaltic pump (ENER TECH electronics Pvt. Ltd.) connected to feed tank as shown in (Fig. 9.10). The microfiltration was done by PVDF MF membrane (pore size 0.45 μm) of coking wastewater to remove the suspended particles.

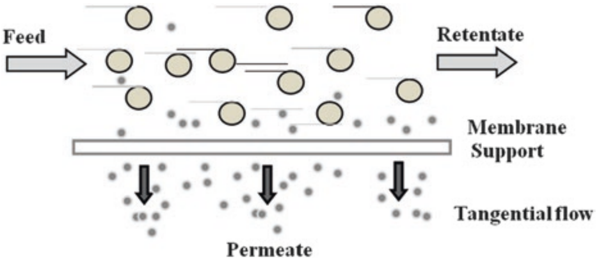


Fig. 9.9 A typical scheme of cross-flow membrane module

Now the clear microfiltrate wastewater used as the feed for NF membranes and approximately 98% phenol and 94% cyanide were rejected while yielding a high flux of 118 L/h at a relatively low pressure of only 15–16 bar at pH of 10. Recovery of 55% of the feed wastewater in concentration mode, negligible variation of rejection and flux was observed. The rest of organic and inorganic pollutants including oil and greases were also rejected by NF1 membrane. Thus, volume reduction of huge quantity of wastewater could be possible with the help of membrane separation, and concentrated pollutants were further degraded by chemical and/or biological treatment (Chandra et al. 2008; Pal et al. 2014a, b; Kumar and Pal 2014).

9.6 Reclamation of Wastewater Using Novel Forward Osmosis-Nano Filtration (FO-NF) System

It is important to end contamination of surface water from industrial or municipal sewer lines by immediate intervention, by the policy makers, and ensure that the reclamation of water from the waste stream is made reusable in the same industry. In this context, membrane technology, such as pressure-driven NF and RO system, stepped in due to their inherent potential to yield reusable water from the waste stream. FO is an emerging system to extract pure water from the wastewater by using low energy and less fouling with a simple design. In this, the feed stream travels parallel to the surface of the semipermeable FO membrane and pure water passes through natural osmosis process using concentrated solution (known as draw

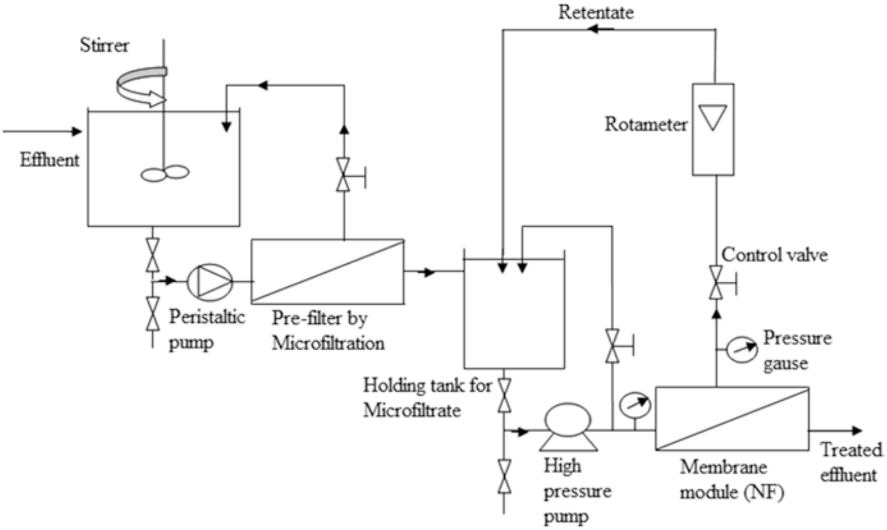


Fig. 9.10 Schematic diagram of cross-flow membrane separation system. (Reprinted from Pal and Kumar (2014) with permission of Taylor and Francis)

solute-DS) flowing counter-current wise in the opposite side of the membrane. FO has attracted more attention in the desalination of the seawater/brackish water, liquid food processing water, landfill leachates, nutrient-rich stream and nuclear plant effluent (Zhao et al. 2012; Phuntsho et al. 2013; Banerjee and De 2010; Fakhru'l-Razi et al. 2009; Kim et al. 2015). The FO system should work in a sustainable and continuous way by providing the feed water and DS of constant composition.

Thus, a periodic discharge of concentrated pollutants present in the coking wastewater (cyanide, phenols, ammonia) is needed which eliminates pollutants, and subsequent treatment is very much necessary during FO to add the fresh COWW. The concentration of diluted DS is again restored by circulating it through NF membrane where pure water is permeated and salt retain back to DS. Different salts may be used as DS such as NaCl, $MgSO_4$, and $CaCl_2$ with concentration of 2–5 M depending upon the concentration of coking wastewater. The high concentration of the DS solution should be maintained to avoid the reverse salt diffusion. To maintain the system in continuous operation, FO-NF system has been proposed where FO loop is present in upstream to extract the water from the polluted water and a downstream loop of cross flow NF membrane module which is used for the recovery of DS while permeating the reusable water as shown in the (Fig. 9.11). Using the novel FO-NF

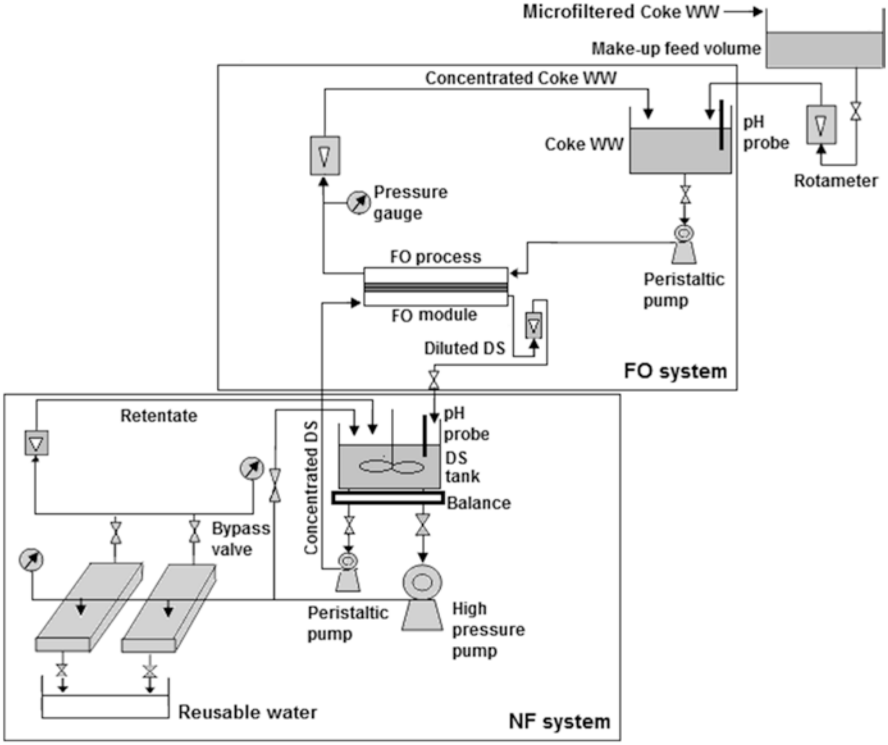


Fig. 9.11 A typical FO-NF system to extract the reusable water from wastewater. (Reprinted from Kumar and Pal (2015a, b) with permission of Elsevier)

system, 45 L/(m^2 h) water flux was obtained using NF1 membrane and 1.5 M NaCl as DS while rejecting almost 99% of all pollutants (Kumar and Pal 2015a, b).

9.7 Membrane-Based Hybrid Treatment System

An advanced treatment technology should be developed for the effective treatment of hazardous pollutants present in the coking wastewater as the conventional treatment technology fails to treat the wastewater up to reusable scale (Kumar and Pal 2012). Membrane-integrated physicochemical and biological treatment approaches have the potential to treat such wastewater into usable water and extract the by-product in the form of struvite (Kumar and Pal 2013a, b). Such scheme has two fold benefits like, on one hand, wastewater will avoid polluting freshwater from toxic contaminants and, on the other hand, save the fresh water consumption.

By applying the logical sequencing of optimized Fenton's treatment, struvite recovery, multiple microbial treatment and final polishing step with membrane separation in an integrated hybrid plant helped to achieve 99% cyanide, 100% phenols and >98% ammonium-N removal (Kumar and Pal 2013c). After cyanide degradation by Fenton's reagent and ammonium-N removal by struvite formation, subsequent biological treatment units are very effective for nitrification and denitrification (Pal et al. 2015). A visual basic simulation software had been developed by membrane-based advanced wastewater treatment plants (Pal et al. 2014a, b). In addition, transport modeling and contingent evaluation has suggested that membrane-integrated physicochemical treatment of COWW could be successful at the industrial scale (Kumar et al. 2015). Composite MF and NF membranes in cross-flow membrane modules could separate the suspended particles and trace ionic contaminants from the treated water, permitting recyclable and reusable grade of water. A typical scheme of membrane-integrated chemical and biological hybrid treatment scheme has been shown in the (Fig. 9.12).

9.8 Conclusions

Today's necessity is to develop a sustainable wastewater management strategy for the treatment of coking wastewater. Coke-making industries consume huge amount of fresh water and generate high strength wastewater heavily loaded with toxic pollutants such as cyanide, thiocyanate, phenols, ammonia, PAHs, oil, and greases. These pollutants are hazardous to the environment and show genotoxic risk to human being. Effective treatment of such industrial effluent has a serious concern for the scientific community. There is need of paradigm shift in treatment regime for such complex wastewater. The novel strategy involves reusing or recycling the waster extracted from the wastewater treatment by applying physicochemical and biological treatment. Such strategies have double benefits as the toxic pollutants

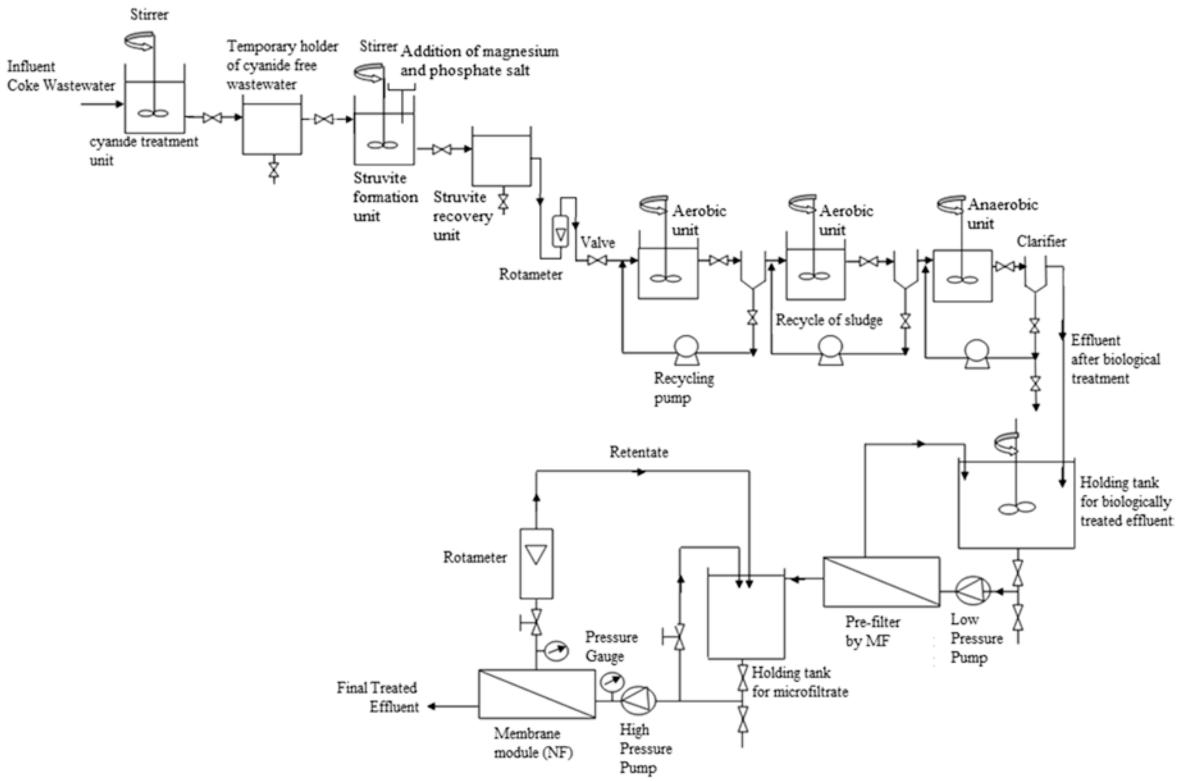


Fig. 9.12 A typical scheme of chemical, biological, and membrane-integrated treatment plant for the treatment of coke-oven wastewater. (Reprinted from Kumar and Pal (2013b) with permission of Elsevier)

will be prevented from contaminating clean water bodies, and this will also cut the consumption of utilizing fresh water.

The chances of success of microbial treatment are very much dependent upon the pre-treatment by chemical methods such as Fenton's treatment for cyanide degradation that lowers down the ammonium-N concentration by struvite precipitation. After optimized chemical process, the downstream nitrification and denitrification units could successfully convert ammonium-N into elemental N. The final micro- and nanofiltration membranes are operated in cross-flow membrane modules, offering long hours fouling free operation without frequent need of replacing the membrane. Such system purifies the chemically and biologically treated coking wastewater up to the level of recycling stage in the same industry which will not only save the fresh water consumption but also protect the surface water from being contaminated.

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Chapter 10
Removal of Organic Pollutants from Contaminated Water Bodies by Using Aquatic Macrophytes Coupled with Bioenergy Production and Carbon Sequestration

Ankit, Lala Saha, Khushbu Kumari, Sagarika Sinha, Nirmali Bordoloi, Jaya Tiwari, John Korstad, and Kuldeep Bauddh

Abstract The burgeoning population and continuous increase in developmental activities are the major cause of rampant release of numerous environmental contaminants. These contaminants pollute the soil, air and water and ultimately enter the food chain. Several physical, chemical and biological techniques have been developed to remove these contaminants; however, these methods are quite costly and not environmentally sound. Specifically, organic contaminants like pesticides, phenols, oils, pharmaceuticals and dyes are entering aquatic habitats and damaging these ecosystems. Application of aquatic macrophytes for the removal of organic contaminants has proved to be an eco-friendly and efficient tool to remediate aquatic ecosystems. Aquatic macrophytes such as *Eichhorn crassipes, Elodea canadensis, Lemna minor, Pistia stratiotes,* and *Trapa natans* can be used for reclamation of contaminated waste and wastewater systems. In addition, these plants help in carbon sequestration, and the biomass of these plants may be used to produce bioenergy (biofuel) at the same time. In this chapter, the potential of aquatic macrophytes for phytoremediation and bioenergy production along with carbon sequestration have been thoroughly discussed.

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10.1 Introduction

Environmental contamination due to anthropogenic sources is widespread and occurs through point as well as diffused sources (Fig. 10.1). However, most of the ecotoxicological implications are often obscure. Environmental contamination is a serious issue grappling the world. The introduction of chemicals, wastewater, wastes, toxic substances, or microorganisms into the air, water, and soil often contributes to areas being unsafe for human habitation, crops being contaminated, water being unpotable, and food being unfit for consumption. Increased concentrations of several organic contaminants like polycyclic aromatic hydrocarbons (PAHs) in the ecosystem have been of great concern owing to its hydrophobicity, toxicity, bioaccumulation, and prolonged presence in living organisms (Yadav et al. 2016; Saxena and Bharagava 2017; Keshavarzifard et al. 2019).

Aquatic ecosystems can be contaminated with hazardous substances such as petroleum hydrocarbons, pesticides, and/or heavy metals that may be toxic to aquatic animals and plants (Fleeger et al. 2003; Singh 2009; Yadav et al. 2017; Mishra and Bharagava 2016). Over consumption of chemicals, fossil fuels, minerals, industrial effluents, and other anthropogenic substances lead to contamination of ecosystems with pesticides, petroleum hydrocarbons, dyes, heavy metals, metal nanoparticles, radionuclides, pharmaceutical products, etc. Aquatic ecosystems are at greatest risk mainly due to imprudent human activities (Borgwardt et al. 2019).

A sustainable technique to remediate polluted aquatic ecosystems is rhizofiltration (Tiwari et al. 2019). It is a type of phytoremediation which involves the use of hydroponically cultivated roots of the plant for remediating contaminated water by absorbing, concentrating, and precipitating the pollutants. Phytoremediation is a green clean technology available for restoring contaminated aquatic ecosystems (Bauddh and Singh 2015a, b; Bauddh et al. 2016a, b; Bharti et al. 2017; Chakravarty et al. 2017; Ashraf et al. 2019; Saxena et al. 2019). Using aquatic plants for the removal of contaminants is proven to be a win-win situation, because first, they are often weeds (not desirable) and second, they are good at extracting contaminants. Macrophytes used for phytoremediation include *Pistia stratiotes, Potamogeton*

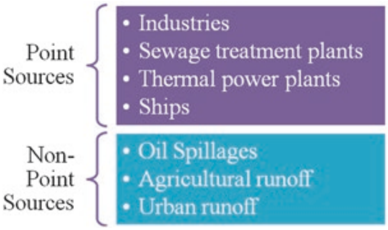

Fig. 10.1 Sources of aquatic ecosystem contamination

pectinatus, Trapa natans, Eichhorn crassipes, Potamogeton lucens, Potamogeton perfoliatus, and Ceratophyllum demersum. The studied macrophytes can efficiently remove heavy metals like Ni, Pb, As, Cu, Cd, and other cations (Kumar et al. 2012; Sood et al. 2012; Sweta et al. 2015; Materac and Sobiecka 2017; Neha et al. 2017; Riaz et al. 2017; Wang et al. 2017).

Carbon sequestration is another ecological service that is provided by aquatic macrophytes. This service is of immense importance because greenhouse gas concentrations are increasing globally. Macrophytes are comparatively bigger in size and have larger biomass than many other aquatic plants and thus have tremendous potential to sequester CO_2. *Typha latifolia* and *Scirpus acutus* are known to have promising potential to sequester carbon (Burke 2011). Aquatic macrophytes also supply biomass for our energy demands. It is a renewable energy that is obtained from living organic material called biomass, which can be used to produce heat, transportation fuels, bio-products and electricity. Using bioenergy can reduce dependency on foreign oil, revitalize rural economies, and supply clean energy, which are all serve vital needs, especially for underdeveloped and developing nations. Aquatic macrophytes like *Lemna* spp. are supportive for producing biofuel (Xu et al. 2011).

10.2 Types of Contaminates Present in Aquatic Ecosystems

Contamination of aquatic environments can be attributed to organic, inorganic and other anthropogenic substances (Fig. 10.2). Industrial sources may be in the form of hot water discharged form a thermal power plant, mine tailings and discharge of heavy metals like Cd, Hg, U, As, and other metals. Agricultural waste can be broadly categorized into organic and inorganic compounds (Milovanovic 2007). Organic compounds include pesticides and oils. There are several classes of pesticides as well, like organochlorine which includes chlordane, methoxychlor, lindane, aldrin,

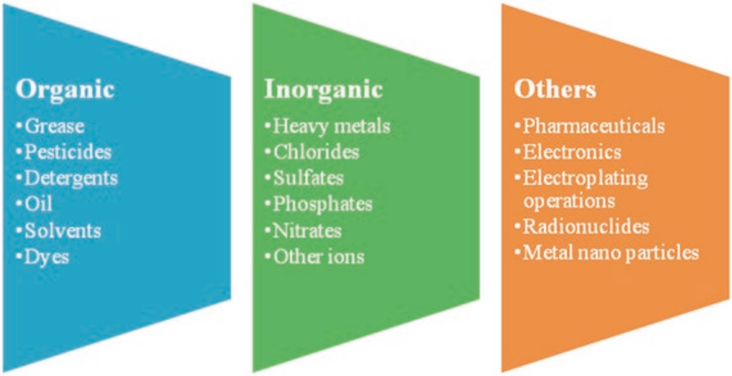

Fig. 10.2 Different classes of aquatic ecosystem contamination

toxaphene, dichloro diphenyl trichloroethane (DDT), heptachlor, endosulfan, and dieldrin. Organophosphates include parathion, malathion, dimethoate and diazinon and carbamates like aldicarb, carbofuran, and carbaryl. Inorganic compounds consist of phosphates, nitrates, and other chemicals (Tiwari et al. 2019). Heavy metals include As from insecticides; chromate and cadmium from electroplating industries; Pb from paint manufacturing pipes and pottery; Hg from combustion of fossil fuels; Cr from leather tanning industry; and Zn from smelting.

10.3 Sources of Organic Pollution

Organic pollutants are mainly emanated from agricultural practices, industrial activities and military waste. Agriculture is mainly based on seed, water, fertilizer and pesticides. Use of pesticides in agricultural activities plays a major role in organic pollution in some urban areas (Ratnakar et al. 2016). Organic pollutants are generally categorized into three groups: (1) organometallic compounds; (2) oxygen, nitrogen, and phosphorus compounds; and (3) hydrocarbons. Hydrocarbons like dioxins, PAHs, and DDT are considered to be the most toxic compounds. Automobiles are a major source of organic pollutants like dioxins, petroleum hydrocarbons, and PAHs and are discharged into the environment in particulate form. Direct disposal of industrial and urban waste into dug pits and improperly constructed landfills contributes to contamination of soil and groundwater adjacent to disposal sites.

Increasing concentration of harmful organic chemicals is mostly due to anthropogenic reasons and is termed persistent organic pollutants (POPs). POPs are toxic organic compounds that are persistent in soils, sediments and biota, have long residence times, and are bioaccumulative (Jacob 2013). POPs like dioxins and dibenzofurans originate from natural sources like volcanic eruptions and forest fires. Some of the major anthropogenic sources of POPs are industrial-based such as agricultural sprays, power stations, heating stations, and evaporation from soil and landfills. Based on application and source, POPs are classified into three groups: pesticide, industrial, and technical chemicals, and also unintended by-products from various industrial activities.

Different types of pesticides such as DDT, aldrin, endrin, dieldrin, chlordane, hexachlorocyclohexane, and toxaphene are used to control weeds, fungi, bacteria, insects, and other organisms. Although agricultural activity is considered to be one of the major sources of pesticide, they are not restricted to agricultural fields. Pesticides are also used as household commodities in the form of powders, sprays, and poisons to kill mosquitoes, cockroaches, fleas, other insects, ticks, and rats. Organic pesticides are semi-volatile in nature and can be dispersed by air and are frequently found in edible items (Jacob 2013). Globally, POPs continue their cycle due to revolatilization from contaminated water bodies, soils, and vegetation.

The most common industrial chemicals are hexachlorobenzene (HCB) and polychlorobiphenyls (PCBs). In the environment, HCB is released from some chlorinated pesticides and chlorinated aromatics, incomplete combustion, waste material, and old disposal sites. PCBs are stable and human-made chlorinated hydrocarbons. PCBs are used in pigments and dyes, plastics and rubber products, fluorescent lighting, floor finish. They enter air, water, and soil during production, use, and improper disposal. Polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs) are unintentional by-products of various chemical processes and combustion which contain chlorine. Important sources of PCDDs and PCDFs are classified into three groups: (1) stationary, which includes chemical industries and thermal processes; (2) diffused, which includes burning of fossil fuels; and (3) secondary, which includes sewage sludge and bio-compost.

10.4 Toxicity of Organic Pollution to Plants and Animals

Persistent organic pollutants generally are low water soluble but highly soluble in lipid and are not naturally degradable. Exposure to POPs can be through food items and environmental exposure; they are highly toxic to plants and animal including humans. POPs are persistent in the environment and contaminate at the origin and also at remarkable distances from the original source of discharge. The negative or unpleasant effects of pesticides include injury to non-target plants and animals. Based on the exposures and time taken for the appearance of toxic symptoms, pesticide toxicity is classified as: (1) acute toxicity, (2) sub-chronic toxicity, (3) chronic toxicity, and (4) delayed toxicity. Excessive application of pesticides in soil may hamper seed germination, crop growth, plant metabolic pathways and interfere with photosynthesis, resulting in subsequent reduction of yield. Fat-soluble pesticides enter animal bodies through the process of biomagnification and accumulate in fatty tissues and remain in food chains for a considerable period of time. Potential health impacts of pesticides include negatively impacting immune, hormonal, nervous, and reproductive system and may cause deformity (DeSolla et al. 2008).

HCB is mobile, persistent, distributed throughout the environment and bioaccumulate and toxic to both humans and biota. HCB can bioaccumulate in fish and other marine animals; a high dose of HCB can lead to birth defects because it affects the reproductive system of animals. Exposure to HCB can occur dermally, through inhalation of polluted air at industrial sites, or by contaminated food. HCB has low to moderate acute toxicity, is immunotoxic and may cause ovarian toxicity; prolonged oral exposure to HCB may cause liver diseases resulting in enzyme induction and porphyria. HCB also affects skin, thyroid glands, bones and nervous systems. HCB toxicity commonly leads to abnormal physical development in young children.

Polychlorinated biphenyls are human-made organic compounds and were first reported as environmental pollutants in 1996. PCBs are released into the environment from hazardous waste sites, burning municipal and industrial waste, and electrical transformers. PCBs tend to bioaccumulate in plant and animal tissues due to their lipophilic nature and can persist in air, water and soil for long periods of time.

Sediments, water, fish and bird tissue have been contaminated by PCB compounds. Plants represent the main entry route of PCBs in food chains. PCBs accumulate in leaf surfaces and other above-ground parts of plants (Campanella et al. 2002). Chronic exposure to PCBs may cause serious immunological, reproductive, neurobehavioral, and endocrine disorders in children. PCBs are suspected to be carcinogenic for animals, including humans (Department of Health and Human Services (DHHS); U.S. Environmental Protection Agency; Pieper and Seeger 2008).

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) are ubiquitous in the environment; human exposure is mainly through diet, inhaling polluted air, and skin contact. PCDD/PCDF comes from air and dust from soil erosion and accumulates in plant above-ground parts. Chronic exposure of PCDDs and PCDFs leads to carcinogenesis; acute toxicity may lead to progressive loss of body weight and hypophagia, gastrointestinal hemorrhage, thymic atrophy, and delayed lethality in tested animals. Chronic exposure of PCDD/PCDF increases the chances of infertility in animals and humans. It can also damage the immune system, causing reproductive and developmental problems, interfere with hormonal functions, and cause kidney and hepatic lesions, which is cancerous (Marcia de 2004).

10.5 Abundance and Ecology of Aquatic Macrophytes

Macrophytes are important biotic components of aquatic ecosystems. Other aquatic life depends on them for food and habitat. Aquatic macrophytes help to control sediment erosion, buffer temperature variation, wave action, stabilize dissolved oxygen, absorb pollutants such as heavy metals and POPs and sequester nutrients. Thus, aquatic macrophytes help maintain healthy aquatic ecosystems.

Aquatic plants can be categorized into seven different groups: Bryophyta (mosses and liverworts), Chlorophyta (green algae), Cyanobacteria (blue–green algae), Pteridophyta (ferns), Rhodophyta (red algae), Spermatophyta (seed-bearing plants), and Xanthophyta (yellow–green algae) (Chambers et al. 2007). Aquatic macrophytes may be floating on the water surface, submerged, or emergent. They can complete their whole life cycle in water or on hydric soils (inundated and non-inundated) (Gecheva et al. 2013). Local habitat determines which macrophytes will grow; it also depends on the availability of light, current velocity, sediment composition and nutrient supply (Hrivnák et al. 2006; Birk and Willby 2010). However, human-impacted land use changes and hydrological dynamics are responsible for aquatic macrophyte diversity (Otahelová et al. 2007). Scarlett and O'Hare (2006) showed that coarse substrate with variable flow of water is suitable for the growth of bryophytes and excludes vascular hydrophytes. Bryophytes are dominant in lotic (moving water) ecosystems, specifically in undisturbed areas (Suren et al. 2000; Scarlett and O'Hare 2006). Thus, bryophytes are good candidates for running water remediation of pollutants.

In many cases, these plants have developed anatomical and morphological adaptations to different habitats. For example, many species like *Nymphaea nouchali*, *Myriophyllum brasiliense*, *Eichhornia crassipes*, *Equisetum fluviatile, Hippuris vulgaris,* and *Potamogeton amplifolius* have floating and aerial leaves to absorb CO_2 directly from the atmosphere. Some species use their root to absorb the high concentration of CO_2 available in the sediments (e.g., *Lobelia* and *Littorella*). These species have modified transport vessels for easy movement of CO_2 from root to leaves, having high root: shoot ratios (Thomaz et al. 2009).

The excessive load of pollutants, such as high nutrient level and essential and nonessential metals, results in booming the macrophytes in aquatic ecosystem. The most common species found in these ecosystems are *Hydrilla verticillata, Eichhornia crassipes*, *Salvinia* sp., *Pistia stratiotes,* and *Phragmities* sp. Although aquatic macrophyte has been utilized in various purposes, their use in eutrophication and for control of the pollution level in water is spreading rapidly. Aquatic macrophyte is used as an environmental filter for treatment of wastewater because of its high growth rate and rapid nutrient assimilation rate. Number of studies have been conducted to find the purification potential of macrophytes and found that there are significant differences among plant species and plant biotopes (e.g., floating leaves, submerged, emergent) (Keskinkan et al. 2003; Kamal et al. 2004; Maine et al. 2004; Victor et al. 2016).

Mostly, the floating macrophytes such as *Pistia stratiotes, Eichornia* spp*.,* and *Salvinia* spp. are used for remediating wastewater, because plant nutrient assimilation and photosynthetic activity are not affected by water turbidity. In addition, floating macrophytes are easier to manage and harvested when needed. The emergent plants such as *Juncus* spp*. and Typha* spp. are efficient enough to adsorb heavy metals to organic matter due to the fast adsorption and their post precipitation as particulate form in the sediment (Thomaz et al. 2009).

10.6 Removal of Organic Contaminants

Removal of organic contaminants by traditional technologies like filtration with coagulation, adsorption, ion exchange, precipitation, coagulation, ozonation, reverse osmosis and oxidation is time taking and costly as well as non-eco-friendly (Chandra et al. 2011; Saxena et al. 2017). Phytoremediation is an important and natural technique for the removal of organic contaminants. Organic contaminants available in the aquatic ecosystem have the potential to remove, sequester, and transform using microphytes (Day and Saunders 2004; Dosnon-Olette et al. 2009; Zhao et al. 2011). Several studies confer that application of aquatic macrophyte to degrade or uptake the organic components organophosphorus, organochlorine compounds, and chlorobenzenes present in water bodies is a cheap and sound technique (Gobas et al. 1991; Gao et al. 2000; Mercado-Borrayo et al. 2015).

The amount of organic compound removed by the macrophytes depends on the availability and composition of contaminates, the biochemical composition of plant tissue and physio-chemical properties of contaminants, as well as aqueous medium (Gao et al. 2000; Gao et al. 2003; Greenway 2007; Rezania et al. 2015). Studies show that halogenated organic compound sequestration by plant occurs through rapid physical and chemical process such as absorption, adsorption, complexation, and reaction with cuticular and membrane components (Nzengung and Jeffers 2001). The capacity to sequester organic contaminants of aquatic plants depends upon the plant's lipid-rich cuticle, which is responsible for sequestration of oils, fats, and hydrocarbons which comes under lipophilic organic compounds (Garrison et al. 2000; Gao et al. 2000; Gao et al. 2003).

10.7 Phytoremediation of Organic Pollutants Using Aquatic Macrophytes

Several common aquatic macrophytes like *Lemna minor, Elodea canadensis, Cabomba aquatica*, *Eichhornia crassipes* are used for the remediation of organic pollutants as shown in Table 10.1. According to Russell (2005), rhizodegradation and phytodegradation are the most suitable and effective removal techniques for organic pollutants, while phytoextraction is best for the removal of inorganic pollutants. Some mechanisms, like phytovolatilization, are equally effective with inorganic and organic contaminants. Phytodegradation process involves various enzymes (e.g., laccase, peroxidase, dehalogenase nitrate reductase, and nitrilase) excreted from the plant roots into rhizosphere which degrade organic molecules, e.g., PAHs (McCutcheon and Schnoor 2003).

However, the uptake of lipophilic large molecules by narrow channels in plant cell wall is difficult. In this case, the oxygenation process serves to enhance the solubility of water and provides an opportunity for conjugation through glycosidic bond formation. Peroxidases, peroxygenases and Cytochrome P450 are involved in plant oxidation of xenobiotics. Other classes of enzymes like carboxylesterases, gluthathione S-transferases are also associated with xenobiotic biotransformation in plant cells (Macek et al. 2000). In addition, the aquatic plant rhizosphere serves as a habitat for many biodegrading microbes and degrades organics much faster.

The organochlorine pesticides (OCPs) are one of the greatest threats to living organisms due to their acute effect and dispersion to long distances and bioaccumulation in the living tissues. Cleaning of the pesticides through conventional methods is expensive and not practical for less contaminated areas specifically in aquatic medium. To overcome the problem, scientist and researchers find that the phytoremediation technique to be more suitable. A number of studies have been conducted to know the phytoremediation potential of different aquatic macrophyte, which has been summarized in Table 10.1. Many studies have been made using *Lemna* spp. to remediate contaminants due to its tolerance in cold, fast growth rate, ease of harvesting, and cost-effectiveness (El-Kheir et al. 2007). A recent study by Xu et al. (2018) found that *P. australis* is a good candidate for remediating chlorpyriphos contamination from the eutrophic water and also indicated that suitable plant combination is needed for treatment of polluted water. Macrophytes like *Eichhornia crassipes* have

Table 10.1 Macrophytes used for removal of different pesticides from aquatic ecosystems

Pesticides	Concentration	Plants used	Removal/accumulation	References
Dimethomorph, copper sulfate, flazasulfuron	Five different conc. Between 0 and 1 mgL^{-1} were exposed to plants	*Cabomba aquatica, Lemna minor, Elodea canadensis*	Order of uptake was *L. minor* > *E. canadensis* > *C. aquatica*. Maximum removal rate as copper sulfate, flazasulfuron, and dimethomorph with 30, 27, and 11 μg g^{-1} fresh weight day^{-1}	Olette et al. (2008)
2,4-D	10 μM concentration used in the experiment	*Lemna minor*	Plants helped in enhancing the microbial degradation process. Sorption also took place passively which helped in depletion of fluoxetine and triclosan	Reinhold et al. (2010)
Chlorpyrifos	The experimental concentrations were 0.0, 0.1 and 0.5 mg L^{-1}	*Pistia stratiotes* *Lemna minor*	The removal conc. was 82 and 87% for *P. stratiotes* and *L. minor* at 0.5 mg L^{-1} conc. level. *L. minor* has high bioconcentration factor than *P. stratiotes*	Prasertsup and Ariyakanon (2011)
Nutrients and chlorpyriphos	The eutrophic water contents 1 mg L^{-1} chlorpyrifos, 10 mg L^{-1} total phosphorus And 30 mg L^{-1} total nitrogen (TN)	*Phragmite australis, Nymphaea alba, M. verticillatum*	*P. australis* found to be suitable for clearing the sediment chlorpyriphos	Xu et al. (2018)
Ethion	The treatment ethion conc. was 1 mg L^{-1} (purity 95%)	*Eichhornia crassipes*	Plant uptake and phytodegradation up to 69%	Xia and Ma (2006)
KHP, sodium tartrate, malathion, 2,4-D	The conc. of organic pollutant present in terms of COD (200, 100, 50, and 25 mg COD L^{-1})	*Eichhornia crassipes*	Study found that maximum absorbance of malathion, 2,4-D, and piroxicam was 67.6%, 58.3%, and 99.1%, respectively	Rodríguez-Espinosa et al. (2018)
Aldrin, Endosulfan γ–HCH DDTs	The available total organochlorine pesticides (OCPs) conc. in the sediments was in the range 3.60–11.12 ng g^{-1}	*Ceratophyllum demersum, Phragmites, Typha*	The OCPs conc. in the plant tissues in between 4.72 and 11.19 ng g^{-1}. The highest conc. is found in *Phragmites* leaves	Guo et al. (2014)

the ability to uptake toxic insecticide like ethion and malathion and degrade up to 68% (Xia and Ma 2006; Rodrigue-espinosa et al. 2018).

The extensive medical facility uses diverse range of medicines and personal care products which have triggered large amount of chemicals. Several studies have demonstrated that with the help of aquatic plants, cleaning of PPCPs is very effective (Table 10.2). Medicinal constituents like ibuprofen, naproxen, and carbamazepine were successfully removed by *Typha* spp. from the contaminated medium with greater than 90% efficiency (Dordio et al. 2010; Zhang et al. 2011). Most of the aquatic plants degrade pharmaceutical products with the help of available microbe.

Apart from the pesticides and pharmaceutical contaminants, there are other types of organic pollutant such as dyes, perchlorate salts (used in food packaging), and phenols which are potentially toxic to living organisms. There are a number of physicochemical methods available like coagulation, adsorption, electrolysis to decolorize and remediate the contaminants from wastewater (Robinson et al. 2001; Aksu 2005), but these methods have drawback because they produce large amount of sludge which results in production of secondary pollutant (Zhang et al. 2004; Al-Degs et al. 2008). Studies have shown that macrophytes like *Lemna minor* and *Eichhornia* can remove up to 90% of organic dyes from the water medium as shown in Table 10.3 (Muthunarayanan et al. 2011; Török et al. 2015; Torbati 2015).

Organic pollutant like phenols which is being released by various manufacturing industries such as fertilizers, plastics, pesticide, and oil refineries into the aquatic ecosystems are said to be extremely dangerous (Huang et al. 2014). A study found that plant degrades phenol by catechol-cleavage pathways where catechol forms (Jha et al. 2013). Catechol further cleaves to produce fumaric and muconic acid which passes to Krebs cycle and finishes the phenol degradation pathway. Recent research found that *Ipomoea aquatica* can be helpful for complete removal of lower concentration (up to 0.05 g/ L^{-1}) of phenol from the water (Lee et al. 2017). Macrophytes sometimes are unable to degrade the contaminant completely, but can transform the toxicants into less harmful compounds (Table 10.4).

10.8 Factors Affecting Phytoremediation of Organic Contaminants by Using Macrophytes

Ecological and physicochemical factors of water, such as light, dissolved oxygen, salinity, temperature, pH, are known to affect the uptake of nutrients or metals or organic pollutants. However, environmental conditions, especially temperature, macronutrients, micronutrients, and non-mineral nutrients significantly affect the macrophytes biochemical composition, which affects the phytoremediation potential (Kalacheva et al. 2002; Juneja et al. 2013). Moreover, the energy derived from photosynthesis and the oxygen released can improve conditions for the absorption of elements.

Table 10.2 Showing PPCPs remediation capacity of different aquatic macrophytes

Pharmaceutical and personal care products (PPCPs)	Concentration	Plant use	(Removal/ accumulation)	References
Carbamazepine (CB), ibuprofelinn (IB), sulfadiazine (DIA), sulfamethoxazole (SMX), sulfamethazone (SMZ) and triclosan (TRI)	High (10 mg L^{-1}) and low (0.8 mg L^{-1}) conc. were considered for the experiment	*Eichhornia crassipes, Pistia stratiotes*	Biodegradation, photodegradation, adsorption and plant uptake occurred synergistically. Removal efficacy was lower in high conc.	Lin and Li (2016)
Ibuprofen, carbamazepine and clofibric acid (CA)	CA, IB, and CB having 97%, 99.8% and >99% purity and wastewater Samples conc. Levels were 0.5,1.5 and 2.5 μg mL^{-1}	*Typha* spp.	Total removal efficiencies of 96%, 97%, and 75% for IB, CB and CA, respectively. It was achieved under summer conditions after 7 days retention time	Dordio et al. (2010)
CB, declofenac, IB and naproxen	Hydraulic residence time of 2–4 days	*Typha angustifolia*	For IB and naproxen removal efficiencies 80% and 91%, in planted beds compared to unplanted beds 60% and 52%, respectively	Zhang et al. (2011)
Tetracycline (TC), and oxytetracycline (OTC)	Plant were put in the experimental flasks/jars, after 8–10 days stock solutions were added	*Myriophyllum aquaticum, Pistia stratiotes*	Both plants have high antibiotic modification rates. Result showed modification rates decreased with increasing OTC concentrations	Gujarathi et al. (2005)
Fluoroquinolones (FQs) (ciprofloxacin (CIP) and norfloxacin (NOR))	CIP and NOR purity of 98.8%. The FQs conc. added for experiment was (10 mg L^{-1})	*Acrostichum aureum L., Rhizophora apiculata*	The antibiotics accumulation occurred in the root parts. Results showed translocation from root to stem and leaves happened at a low rate. Overall a good candidate for phytoremediation	Hoang et al. (2013)
Methyl (MeP) and propyl parabens (PrP)	___	*Landoltia punctate, Lemna minor*	For MeP and PrP average removal efficiency was 90 and 89%, respectively	Anjos et al. (2018)

(continued)

Table 10.2 (continued)

Pharmaceutical and personal care products (PPCPs)	Concentration	Plant use	(Removal/ accumulation)	References
Fluoxetine, ibuprofen and triclosan	10 µM concentration used in the experiment	*Lemna minor*	Plants helped in enhancing the microbial degradation process. Sorption also took place passively which helped in depletion of fluoxetine and triclosan	Reinhold et a. (2010)
Atrazine	Atrazine used conc. was 4.0 mg L^{-1} in the study	*Acorus calamus, Iris pseudacorus, Lythrum salicaria*	The degradation capacity of *A. calamus, I. pseudacorus,* and *L. salicaria* were recorded 61.8, 75.6, and 65.5%	Wang et al. (2012)

Table 10.3 Macrophytes used for removal of dyes

Dyes	Concentration	Plant use	Removal/ accumulation)	References
Azo dye (AB92)	The conc. of dye used for the study was between 5 and 20 mg L^{-1}	*Lemna minor*	Study confirmed that *L. minor* had considerable potential for remediate AB92	Khataee et al. (2012)
Triphenylmethane dyes (crystal violet and malachite green)	The experimental conc. was 1 g dye/1 L	*Lemna minor*	Crystal violet removed by 80% and malachite green by 90%	Török et al. (2015)
Malachite green	Dye concentrations use between 5 and 40 mg L^{-1}	*Lemna minor*	Decolorization ability of the plant was 88%	Torbati (2015)
Red RB and black B (dye)	The test conc. was ranging from 10, 20, 30, 40 and 50 ppm	*Eichhornia crassipes*	Successfully degrade the red RB (95%) and black B (99.5%)	Muthunarayanan et al. (2011)

10.8.1 pH of Growing Medium

Growth and biomass of the plants are two important factors for a phytoremediator species. The pH is one of the most important factors for cultivating macrophytes because it can control the solubility and availability of CO_2 and essential nutrients which affect the growth of plants. The change in pH lowers the plant growth and metabolic inhibition (Juneja et al. 2013). Shah et al. (2014) conducted a study to see the effect of pH on the performance of aquatic macrophytes at different pH values

Table 10.4 Macrophytes used to remove other organic contaminants

Others organic pollutants	Concentration	Plant use	(Removal/accumulation)	References
Organic matter and nutrients	Maximum organic load was 6.16 g BOD/ m^2day	*Phragmite karka, Vetiveria zizanioide*	*V. zizanioide* had better removal capacity (TSS: 92.3%; BOD5: 92.0%; PO4 3−: 86.7%) than *P. karka* (91.3%, 90.5%, 85.6%). In addition, *P. karka* removal efficiency was better of NH4 $^+$ (86%), NO3 − (81.8%) and SO4 2− (91.7%) than *V. zizanioide* (83.4%, 81.3%, 90.5%)	Angassa et al. (2018)
Phenols	The test medium conc. of phenol was 0.05, 0.10, 0.20, 0.30 and 0.40 g/L^{-1}	*Ipomoea aquatica*	Plants completely removed the phenol conc. 0.05 g/L^{-1} after 12 days of growing. Plant extract test showed *I. aquatica* was able to degrade the absorbed phenol	Lee et al. (2017)
Perchlorate	Examined in sand and aqueous medium with test sample conc. between 0.2 and 20 ppm	*Myriophyllum aquaticum*	Five times higher uptake rates in aqueous medium than in sand medium. Phytotransformation occurred with accumulation of perchlorate in the plant tissues (1.2 g/kg) was recorded	Susarla et al. (1999)
Phenanthrene	The contaminants conc. was 0.385 mg L^{-1}	*Scirpus lacustris, Typha* spp.	99.9% phenanthrene adsorption took place	Machate et al. (1997)

and found almost very poor performance at pH below 5 and above 10. Maximum performance was observed at pH 7.5. Therefore, pH between 6 and 9 was recommended as the most suitable pH for better growth of the macrophytes. Lu et al. (2004) observed the best growth of water hyacinth in the pH range of 5.5–7.0 (El-Gendy et al. 2006).

10.8.2 Temperature

Temperature is another most important environmental factor that influences the macrophytes' growth pattern, biochemical composition, cell size, and nutrient supplies (Table 10.5). Studies have been conducted to know the performance of macrophytes under different temperature conditions. Shah et al. (2014) conducted an experiment on three macrophyte species (Water hyacinth, Duckweed and Water lettuce). These macrophytes were found to be temperature sensitive and showed no

Table 10.5 Impact of temperature on different macrophytes

Aquatic plants	Results	References
Water hyacinth (*Eicchornia crassipes*)	Water hyacinth was reported to be very sensitive to temperature, and 15–25 °C was found to be the most favorable temperature for their optimum growth	Wang et al. (2013)
Salvinia natans, Ceratophyllum demersum	In this experiment, *ceratophyllum demersum* was found to be more tolerant to temperature change than *salvinia natans* which renders it more effective in phytoremediation	Hreeb (2017)
Eelgrass *(Zostera marina)*	The optimum water temperature for eelgrass appeared to be between 10 and 20 °C. These results show that extreme conditions may affect the fitness and ecological performance of eelgrass	Nejrup and Pedersen (2008)

growth and removal of pollutant at temperature below 10 °C. Almost all three species ceased to survive at such low temperature. There was no growth of these macrophytes; therefore, there was negligible uptake of nutrients (N and P) by the plants. It was also observed that the temperature between 15 and 38 °C is suitable for the treatment of municipal wastewater by macrophytes as optimum growth was observed in this temperature range. Majority of the aquatic macrophytes are temperature sensitive and not suitable for temperate or frigid areas.

10.8.3 Plant Species

Albers and Camardese (1993) found submerged species to be more efficient in phytoremediation because of high accumulation of the contaminants as compared to emerged species. This might be due to degradation and disappearance of plant's roots such as *Ceratophyllum demersum*, which do not have profound root system but develop modified leaves with a root-like appearance and their waxy coat inhibits absorption by epidermal cells (Yurukova and Kochev 1994). In another study, due to specific morphology and higher growth rate, free-floating plants were more efficient to heavy metal uptake in comparison with submerged and emergent plants. However, the removal efficiency is highly correlated with growth rate, tolerance to higher concentration of metals, and adaptability to different environmental conditions (Rezania et al. 2016).

10.9 Carbon Sequestration Potential of Macrophytes

For the last 200 years, the levels of greenhouse gas (GHGs) especially CO_2 has increased palpably in the atmosphere. The global desire to reduce GHGs levels has led to an increase in the number of researches in the field of carbon sequestration.

Macrophytes being greater in size and obviously having larger biomass than other aquatic plants have comparatively greater potential to sequester carbon especially in the form of CO_2.

Some of the emergent macrophytes like *Typha latifolia* and *Scirpus acutus* are seen to have good potential to promote the process of carbon sequestration (Burke 2011). Biological fixation of light energy into chemical energy, the process known as photosynthesis is the process by which plants transform atmospheric carbon as CO_2 into the carbon of biomass or plant tissue. Accurate knowledge of species-specific carbon contained in biomass of plant is indispensable for better understanding of carbon stock of a particular ecosystem (Thomas and Martin 2012). A study was done by Maqbool and Khan (2013), by taking into account several macrophytes for their organic carbon percentage. The percentage of carbon varied between 34.97 and 50.92% as shown in Fig. 10.3.

Wetland ecosystems are really unique because they are biologically diverse and have local economic benefits (Goswami et al. 2010). This is supported by the fact that even a eutrophic system colonized by only water hyacinth can trap significant amount of carbon. The net primary productivity (NPP) of a wetland is remarkably higher than many terrestrial ecosystems (Reddy and DeLaune 2008), and so, wetlands are very important as sinks of carbon sequestration.

A number of factors affect the rate of carbon sequestration. With increase in temperature, the rate of respiration is increased, which in turn can decrease the rate of carbon sequestration (Turnbull et al. 2001), also shorter day length, lower temperature, and low light intensity, the rate of photosynthesis (Yamasaki et al. 2002) as well as enzyme activity (Khodorova and Boitel-Conti 2013) may go down, all these factors might be limiting the efficiency of carbon capture by the plants. It can

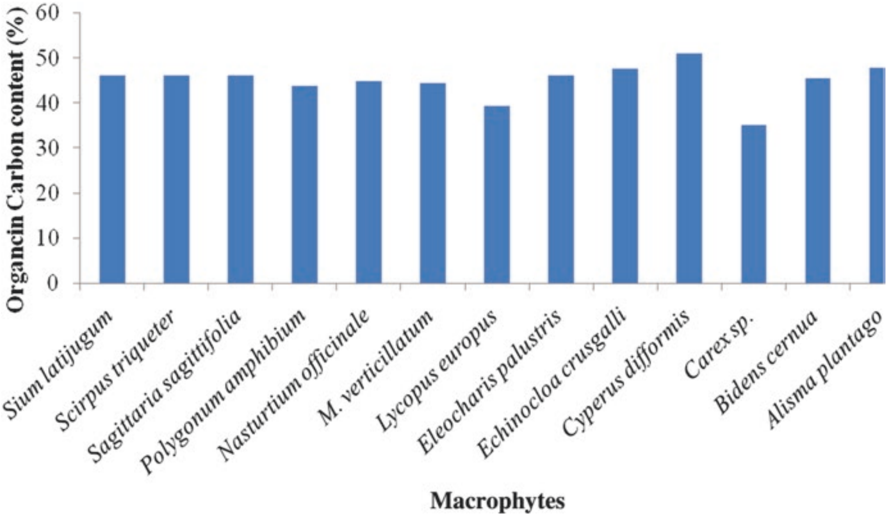

Fig. 10.3 Organic carbon content (percentage) of different species of macrophytes in Lake Manasbal. (*Source*: Maqbool and Khan 2013)

be concluded that macrophytes are an inseparable constituent of aquatic ecosystems. Besides playing several important roles in numerous accessory resilience, restoration capacity, etc., it also plays an important role in carbon capture, and they also are significantly sustainable and promising means of sequestering atmospheric carbon.

10.10 Biofuel Production by Macrophytes

Like algae, macrophytes also perform the dual role of wastewater treatment along with the production of renewable fuels. Macrophytes are known to absorb important wastewater nutrients like phosphorus and ammonium. On analyzing the pyrolysis products, it was found that algae and Azolla produce bio-oils of similar range which consist of a wide spectrum of photochemicals that include C_{10}–C_{21} alkenes that can be directly utilized as supplement for biodiesel fuel as given in Table 10.6 (Muradov et al. 2014).

Lemna spp. or duckweeds have comparatively high level of starch, lower lignin level, and the composition of cell wall carbohydrates help improve the production of bioethanol, in an economical way. Its production is 50% more as compared to production of ethanol based on maize, and this makes duckweed more competitive for the production of ethanol (Xu et al. 2011). Aquatic macrophytes like *Eichhornia crassipes, Nymphaea* spp., and *Eichhornia azurea* have double whammy, as they are invasive as well as they cause environmental problems like excessive growth (Villamagna and Murphy 2010; Luo et al. 2011; Pal et al. 2017), thereby obstructing the passage of light for submerged plants and reducing the level of oxygen in water.

Table 10.6 Different methods of bioenergy production from various macrophytes

Source of bioenergy	Process of bioenergy production	References
Bioethanol production	1. Hydrolysis 2. Fermentation	Patel and Patel (2015), Randive et al. (2015)
Lipid production	1. Solvent extraction (a) Chloroform based (production at laboratory scale) (b) Hexane based (production at industrial scale)	Halim et al. (2012)
Biogas production	1. Biomass conversion into slurry followed by anaerobic digestion	Malik (2007)
Biohydrogen production	1. Biological water–gas shift reaction 2. Photo fermentation 3. Dark fermentation 4. Direct photobiolysis 5. Indirect photobiolysis	Gaudernack (1998), Lin and Jo (2003), Levin et al. (2004), Bridgwater (1999)

However, these plants can be effectively used for the production of second-generation biofuel by pyrolysis. The fuel thus obtained is mainly composed of alkanes (~26%) (Lu et al. 2009).

Using aquatic invasive plant species for the production of biofuels have multiple ecological benefits; some of them have been enumerated below:

(a) They grow and accumulate rapidly thus producing enormous biomass (Wilkie and Evans 2010).
(b) As they are invasive, they do not have an impact on the production of food.
(c) Energy dispersive X-ray fluorescence spectrometry (EDX) analyses of ashes show significant levels of micro and macronutrients, which may be incorporated in biochars, indicating that they can also be used in soil management (Santos et al. 2018).

Using different invasive aquatic species have unique benefits, such as water hyacinth has the following ecological benefits: (1) no/low maintenance cost, (2) its biomass is of non-food nature, (3) rapid reproduction rate, (4) does not require land use change, (5) highly energetic biomass (Das and Jana 2003), (6) low lignin and high cellulose and hemi cellulose content (Bergier et al. 2012), (7) resistant to insect, pests, and diseases (Bhattacharya and Kumar 2010).

Using Azolla has a different set of ecological benefits altogether, which has been enumerated below: (1) it has high productivity, (2) it can grow abundantly even in wastewaters, (3) unique chemical composition makes Azolla sustainable, attractive, and universal feedstock, (4) low energy demand for proliferation, (5) almost zero maintenance system makes it a renewable biofuel source of choice (Miranda et al. 2016). Using invasive species like *Eichhornia crassipes, Nymphaea* spp., *Eichhornia azurea,* for the production of biodiesel is thus a win-win situation.

Apart from this, the biomass of *Eichhornia azurea, Eichhornia crassipes, Salvinia,* and *Pistia stratiotes* can also be used to produce biogas. The biogas may be obtained by the process of anaerobic digestion. The biogas thus obtained has significant amount of methane (CH_4). The amount of methane in the biogas obtained from the mixture of these plants in volume percentages on 7 days, 14 days, 21 days, and 28 days are 40.9%, 49.7%, 48.0%, and 48%, respectively (Pereira and de Jesus 2011).

The most common method for the production of biogas from aquatic plants includes the processing of wet biomass into slurry that is ultimately loaded into an anaerobic digester (Malik 2007). Some factors that generally affect biogas yield from aquatic plant biomass are as follows (Wilkie and Evans 2010): (1) particle size, (2) volatile solid content, (3) trace nutrients, and (4) inoculation—need of the hour is to develop harvester machines and processing infrastructure that can transport these aquatic plant biomasses to refineries in timely and cost-effective manner.

10.11 Conclusion

The presence of organic contaminants in aquatic ecosystems are a global concern and their safely removal is a pivotal task. Application of aquatic macrophytes for the removal of these contaminants may be done in an environmentally manner through the process, phytodegradation/phytovolatilization. The macrophytes like *Elodea canadensis, Lemna minor, Eichhorn crassipes, Trapa natans*, *Pistia stratiotes* may be used for the removal of organic contaminants. Majority of macrophytes are high biomass-producing plants, and therefore, the biomass may be used for the energy production (as biofuel). Several potential phytoremediator macrophytes like *Eichhornia crassipes*, *Typha angustifolia* are also considered as significant carbon sequesters (Pal et al. 2017). Therefore, the application of aquatic macrophytes for the remediation of organic pollutants may also help in management of another two major environmental issues, i.e., energy crisis and global climate change.

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Chapter 11
Biopolymers and Their Application in Wastewater Treatment

Jyoti Pandey

Abstract Due to heavy industrialization and urbanization, the conservation of the environment has become increasingly important in view of the raised ecological problems. The discharge of huge quantities of effluents from industries and municipalities into rivers and lakes makes the condition vulnerable for sustainable life. The presence of organic toxics such as dyes and heavy metals, such as chromium, mercury, cadmium, cobalt, copper, nickel, lead, zinc and tin, in our water resources may cause serious health hazards to living organisms. Various technologies for removal of toxic chemicals and ions from industrial and agricultural effluents have been introduced such as adsorption, coagulation, flocculation, precipitation, co-precipitation, solvent extraction, ion exchange and membrane technology. However, most of these techniques require synthetic toxic reagents which are expensive too and hence the capital cost for treatment increases. The wide availability, biodegradability, non-toxicity and relatively inexpensiveness of biopolymers present an attractive alternative to such toxic synthetic and chemical products. In this context, several biopolymers were chemically refined to work as cationic or anionic agents for wastewater treatment. The book chapter summarizes the research carried out on the use of biopolymers to remove heavy metal and toxic chemicals from solutions and effluents. The various biopolymers (e.g. cellulose, chitosan, tannin, alginate, gums and mucilage), their classification, mechanisms of action, factors and their application in wastewater treatment in the scientific literature are analysed and compiled.

Keywords Industries · Wastewater · Biopolymers · Application · Treatment

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11.1 Introduction

Water is the most important and essential element on the mother earth for sustainable life. Alarming growth in population, urbanization, industrialization, agricultural activities, climate change and socio-economic growths, along with high living standards, have generated ever-lasting demands for water resources (Kishor et al. 2019; Zainith et al. 2019). However, due to this heavy population load and human activities, quality of our water resources is deteriorating continuously (Bharagava et al. 2008; Chandra et al. 2009). Every year, millions of tons of different types of wastes such as industrial sewage water containing thousands of organic (fertilizers, pesticides, detergents, plasticizers, pharmaceuticals, hydrocarbons, biphenyls, phenols, oils, greases), inorganic (heavy metals, compound containing, fluoride, phosphate, sulfate, nitrate) and biological pollutants or contaminants (virus, bacteria, fungi, algae, amoebas and planktons) have been released into our water resources (Bharagava et al. 2018; Saxena et al. 2019). Such kind of introduction of pollutants or contaminants from industrial, agricultural and natural disposals to our water resources is a major environmental and health concern (Bharagava and Chandra 2010; Kishor et al. 2019). In this regard, water treatment plays a significant role in improving public health and environmental quality.

Several methods have been developed and applied for water and wastewater treatment including precipitation, co-precipitation, solvent extraction, adsorption, coagulation, flocculation, ion exchange and membrane technology (Patterson 1989; Brooks 1991; Chmielewski et al. 1997; Blais et al. 1999). These methods are exploited to reduce pollutants or contaminants from industrial wastewater and to remove toxic chemicals from sewage including municipal sanitary sewers and to recover the quality of raw drinking water. Most of these methods have utilized inorganic compounds, e.g. alum and $FeCl_3$, or organic polymers, e.g. polyacrylamides, which have their own benefits and drawbacks when their applicability and pollutant remediation efficacy is considered (Ahmad et al. 2008; Ashraf et al. 2013a).

In recent years, biopolymers illustrate an attractive alternative to synthetic inorganic and organic compounds because of following properties (Bolto and Gregory 2007):

1. Abundance and cheap resource make biopolymers economically viable.
2. The presence of large number of active functional groups such as amino and hydroxyl groups which increases adsorption capacity of biopolymers for many pollutants or contaminants.
3. Tendency to get modified through physical or chemical methods for more versatile applications.
4. They are safe, biodegradable, non-toxic and environment-friendly in nature.

In addition to above properties, the sludge obtained after wastewater treatment by biopolymers can be efficiently degraded by microorganisms due to its biodegradable nature (Renault et al., 2009a). Adsorption, coagulation and flocculation are the main methods applied by the biopolymers for water and wastewater treatment. The adsorption capacity of biopolymers is an important parameter for disposing of many kinds of pollutants from waste or polluted water. The availability of a wide range of biopolymer-based adsorbents and their ease of operation makes this method most popular among all the methods available for wastewater treatment.

In coagulation or flocculation methods biopolymers can destabilize the large colloidal particles by increasing the ionic strength and decreasing the zeta potential so that there is a significant decrease in the thickness of the diffuse part of the electrical double layer that takes place. In another way, biopolymers with macromolecular structures and a variety of functional groups (e.g. carboxyl and hydroxyl groups) can interact with contaminants by adsorbing counter ions and neutralize the particle charge (Özacar and Şengil 2003). For many years, several biopolymers such as tannins, cellulose, alginate, chitosan, gums and mucilage have been attracting wide interest of researchers for developing advanced adsorbents and flocculants for wastewater treatment. In this context, herein we summarize all the aspects of biopolymers along with their role in water treatment.

11.2 Biopolymers and Their Classification

Biopolymer is a new generation polymeric material. These polymers are made up of covalently bonded monomeric units which form chain-like arrangement of molecules. The prefix 'bio' denotes its natural origin and biodegradable nature of biopolymers. Biopolymers are environment-friendly molecules which can be degraded by naturally occurring organisms; only organic by-products such as carbon dioxide and water are generated which have no harmful effect on the environment. The versatile nature of biopolymers such as biodegradability, renewability and abundance makes biopolymers an attractive alternative material to petroleum-derived plastics. The broad classification of biopolymers is shown in Fig. 11.1 (Vieira et al. 2011).

Several biopolymers are of both bio-based and fuel-based origin such as PTT, PBS and PLA, although PLA is mainly produced by fermentation from renewable resources such as sugar cane and starch and can also be synthesized from fossil fuels.

11.3 Mechanism of Action of Biopolymers for Wastewater Treatment

11.3.1 *By Bridge Formation*

Polymer bridge formation takes place when long chain polymers with high molecular weight and low charge density are adsorbed onto the surface of more than one particle in such a way that long loops and tails extend or stretch some way into solution and thus these 'hanging' polymeric segments create 'bridging' between particles (Fig. 11.2) (Lee et al. 2012; Caskey and Primus 1986; Biggs et al. 2000;

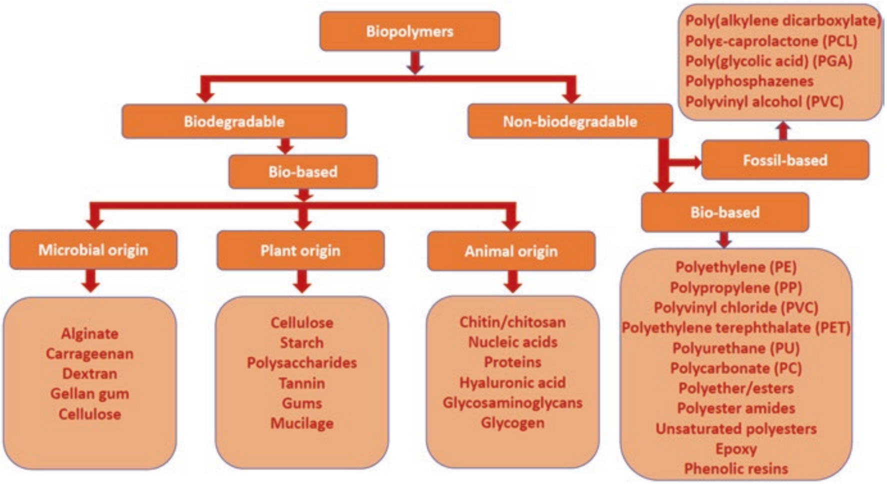


Fig. 11.1 Broad classification of biopolymer

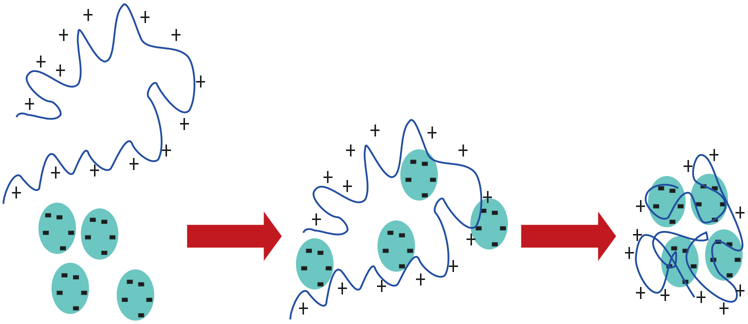


Fig. 11.2 Mechanism of bridge formation

Blanco et al. 2002). The long polymeric chains which can extend from one particle surface to another are required for effective bridging (Razali et al. 2011). In addition, there should be enough unoccupied surface on a particle for attachment of polymeric chains adsorbed on other particles. In general, for bridge formation an excessive amount of polymer is required; otherwise the particle surfaces will be exaggeratedly coated with polymer and no vacant sites will be available to ‘bridge’ with other particles (Fig. 11.2) (Sher et al., 2013). However, the adsorbed amount should not be too low because it will cause lesser number of bridge formation. In this way, it has been well established that polymer bridging provides much larger and stronger flocks than those formed in other ways.

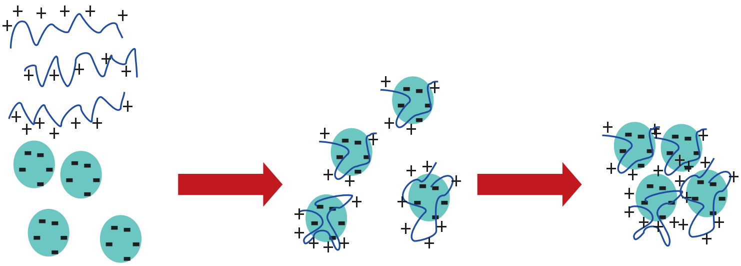


Fig. 11.3 Mechanism for electrostatic patch

11.3.2 By Electrostatic Patch

When bridging capability of long chain polymer is reduced, another possibility arises, which is known as 'electrostatic patch' mechanism (Fig. 11.3). The basic idea behind 'electrostatic patch' mechanism is that, when a highly charged cationic polymer adsorbs on a negatively charged surface, it is not physically possible for every negatively charged site on the surface to get neutralized by a cationic polymer chain (Blanco et al. 2002). This results into the formation of cationic 'patches' or 'islands' on negatively charged surfaces. The importance of 'patchwise' adsorption is that, as particles approach closely, strong electrostatic attraction between positive patches and negative zones occurred which can give rise to particle attachment (Bolto and Gregory 2007).

11.3.3 By Adsorption

Adsorption is a surface phenomenon where one or more adsorbates are attracted towards the adsorbent with which they are in interaction and bonded to its surface through liquid-solid intermolecular forces of attraction and get deposited at the solid surface (Fig. 11.4). It follows common mechanism for inorganic and organic pollutant removal. The adsorption phenomenon can be categorized as: (1) physisorption (involving weak van der Waals forces), (2) chemisorption (involving covalent bonding) or electrostatic sorption (involving ionic bonding) (Ashraf et al. 2013b).

As the adsorption proceeds, an equilibrium is established for adsorption of the solute between the solution and adsorbent. At equilibrium, the adsorption amount of adsorbate (q_e, mmol g^{-1}) can be calculated according to the following Eq. (11.1):

$$q_e = V\left(C_0 - C_e\right) / M \qquad (11.1)$$

where V is the volume of solution (L), M is mass of monolithic adsorbents (g), C_0 is the initial adsorbate concentrations and C_e is the equilibrium adsorbate concentrations.

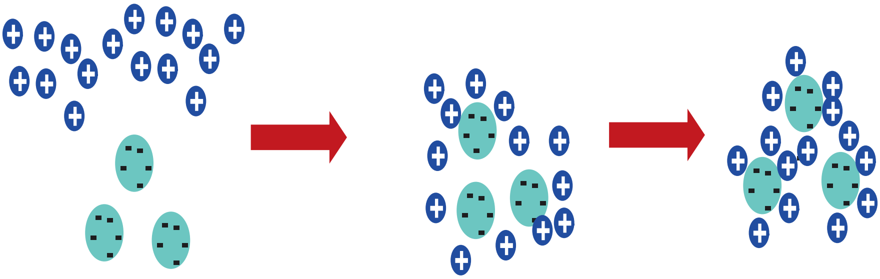


Fig. 11.4 Mechanism of adsorption

11.3.4 By Coagulation/Flocculation

Coagulation/flocculation is one of the most widely used solid-liquid separation processes which involve the removal of all kind of solids (suspended and dissolved) and colloidal and organic contaminants present in industrial wastewater (Renault et al. 2009b). Coagulation process involves charge neutralization which weakens colloidal matter and aggregates finely divided or dispersed particles into large masses (Fig. 11.5). These large masses adsorb dissolved organic substances by an adsorption mechanism and can easily be eliminated by simple filtration and sedimentation (Sharma et al. 2006). These methods are simple and efficient for wastewater treatment and have found extensive application for the treatment of different types of wastewater (Yue et al. 2008; Ahmad et al. 2005; Tatsi et al. 2003; Wong et al. 2006; Zhong et al. 2003).

11.4 Effect of Factors on Efficacy of Biopolymers

11.4.1 Effect of pH

pH is identified as one of the most important parameters to judge the efficacy of biopolymers. The role of biopolymers in wastewater treatment is strongly dependent on pH, as it can affect the extent of positive or negative charge on the polymeric surface. For example, chitosan is a weak base and its dissociation equilibrium is represented by Eq. (11.2):

$$\text{Chitosan}-\text{NH}_3{}^+ + \text{H}_2\text{O} \leftrightarrow \text{Chitosan}-\text{NH}_2 + \text{H}_3\text{O}^+ \tag{11.2}$$

Its dissociation equilibrium constant is given by Eq. (11.3):

$$K_\text{a} = \left[\text{Chitosan}-\text{NH}_2\right]\left[\text{H}_3\text{O}^+\right] / \left[\text{Chitosan}-\text{NH}_3{}^+\right] \tag{11.3}$$

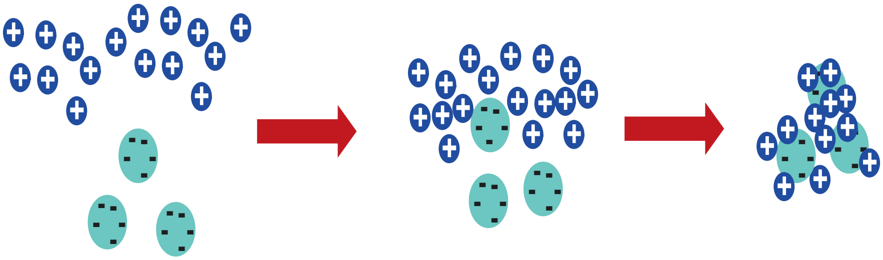


Fig. 11.5 Mechanism of coagulation

In acidic solutions, protonation of amine groups of chitosan is controlled by the p*K*a value and regulated by the charge density and extent of deacetylation (Guibal 2004). In general, p*K*a values fluctuate between 6.3 and 7.2 which directly depend on the extent of deacetylation (Sorlier et al. 2001) and are helpful in understanding the electrostatic interactions of chitosan with cations and anions. Equation (11.2) clearly depicts the effect of pH on the generation of ammonium groups ($–NH_3^+$). At neutral pH, approximately 50% of the total amino group of chitosan is protonated (Guibal, 2004). At particular pH when the protonation of amino groups is high, the tendency to adsorb metal anions is also increased (Ashraf et al., 2012). The overall number of protonated amino groups declines by increasing the pH level, and then the tendency towards metallic cations increases.

11.4.2 Effect of Size

The efficiency of biopolymers mainly depends on their physico-chemical characteristics such as porosity, surface area and particle size of biopolymer. In general, biopolymers in their native form are non-porous and possess low surface area; e.g. chitosan has a very low specific area ranging between 2 and 30 $m^2 g^{-1}$. Modification of biopolymer either by crosslinking or by grafting increases its adsorption performances (Chiou and Li 2002; Ruiz et al. 2000; Delval et al. 2003). In general, adsorption capacity varies in irregular manner on variation in the particle size (Delval et al. 2003). The adsorption or flocculation increases with decrease in size of the particle as the effective surface area is quite high for the same mass of smaller particles, and hence the time required to achieve the equilibrium significantly increases with the size of biopolymer. The influence of this parameter also depends on several other factors such as the chemistry of the pollutant, the physiochemical characteristics of the biopolymer such as its crystallinity, the degree of crosslinking and the rigidity of the polymeric chains (Ruiz et al. 2000).

11.4.3 Effect of Dose of Biopolymers

In general, the removal efficiency of biopolymers improved by increasing its dosage. This is due to the fact that the higher dose of biopolymers in the solution provides greater availability of exchangeable sites for the metal ions and pollutants. However, after a certain dose of biopolymer, the maximum adsorption is achieved and an equilibrium is established between bounded and unbounded free ions in the solution. On attainment of equilibrium, the concentration of free ions remains constant even with further addition of the dose of biopolymer (Ramya et al. 2011).

11.4.4 Effect of Contact Time

Generally, at the beginning of the treatment, the removal rate of metal ions increases with increase in contact time. Afterwards removal rate slowed down and equilibrium is achieved. Therefore, equilibrium time is among the important parameters responsible for an economical wastewater treatment system (Ramya et al. 2011).

11.4.5 Effect of Temperature

The adsorption capacities of biopolymer increase with increasing temperature. This phenomenon is quite common among biopolymer-based adsorbent and is due to the fact that increasing temperature not only increases the mobility of the ions, but may also produce a swelling effect within the internal structure of the biopolymer. However, after optimum temperature the number of adsorbed ions on adsorbent decreases due to the predominance of desorption step (Wong et al. 2008).

11.5 Biopolymers for Wastewater Treatment

The wastewater produced from various types of industries contains large amount of fine suspended and dissolved solids, organic and inorganic matter, metals and toxic chemicals. Various traditional and advanced technologies have been utilized to remove such impurities from wastewater, such as precipitation, ion exchange, solvent extraction, membrane filtration, adsorption, coagulation, flocculation and electrolytic and biological methods (Radoiu et al. 2004). Among these methods, adsorption, coagulation and flocculation are the most widely used separation process for the removal of heavy toxic metals and chemicals, suspended and dissolved solids and colloids present in industrial wastewater (Renault et al. 2009b). These are simple and efficient methods for wastewater treatment and have found extensive application in wastewater treatment.

Over the past few decades, several research studies have been pursued to develop cost-effective and easily available biopolymer-based adsorbent, flocculant and coagulant for wastewater treatment. Chitosan, cellulose, alginates, tannins, gum and mucilage are some well-known biopolymers that have attracted wide interest of researchers for the development of efficient materials for water treatment. In this section, we will discuss these biopolymers and their derivatives that have been developed to increase their efficacy in removal of toxic chemicals and heavy metals from wastewater.

11.5.1 Chitosan

Chitosan is a linear amino-polysaccharide containing *N*-glucosamine and *N*-acetyl-D-glucosamine monomeric units (Fig. 11.6). The arrangement and distribution of these two monomeric units along the chain determine the physical, chemical and biological properties of the biopolymer (Anitha et al. 2014).

Chitosan is obtained from the alkaline deacetylation of chitin, a biopolymer extracted from crustaceans, arthropods, fungi, bacteria and other organisms (Rinaudo 2006; Yen and Mau 2007) as shown in Fig. 11.7.

Deacetylation exposes the amine groups responsible for its cationic behaviour and necessarily required for adsorption (Jaafari et al. 2004). Chitosan has found extensive application in various fields due to its cationic behaviour and serving as most promising biopolymer for the development of new materials. The availability of free amine groups determines the solubility of chitosan; in general, chitosan is insoluble in water and organic solvents but soluble in dilute weak organic acids such as acetic acid and formic acid (Renault et al. 2009a; Szyguła et al. 2009). At acidic pH the free amino groups of chitosan are completely protonated and provide high charge density (Rinaudo 2006; Guibal and Roussy 2007) to the cationic biopolymer. Thus, acidic solution of chitosan produces protonated amine groups along the chain and facilitates electrostatic interactions with anionic contaminants such as dyes, heavy metal anions, toxic organic compounds, etc. (Guibal et al. 2006; Renault et al. 2009a; No and Meyers 2000), and makes it effective for wastewater treatment.

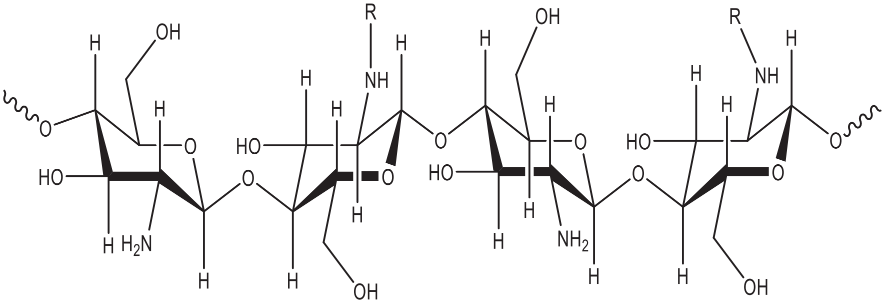


Fig. 11.6 Structure of chitosan, where R=Ac or H depending on the degree of acetylation

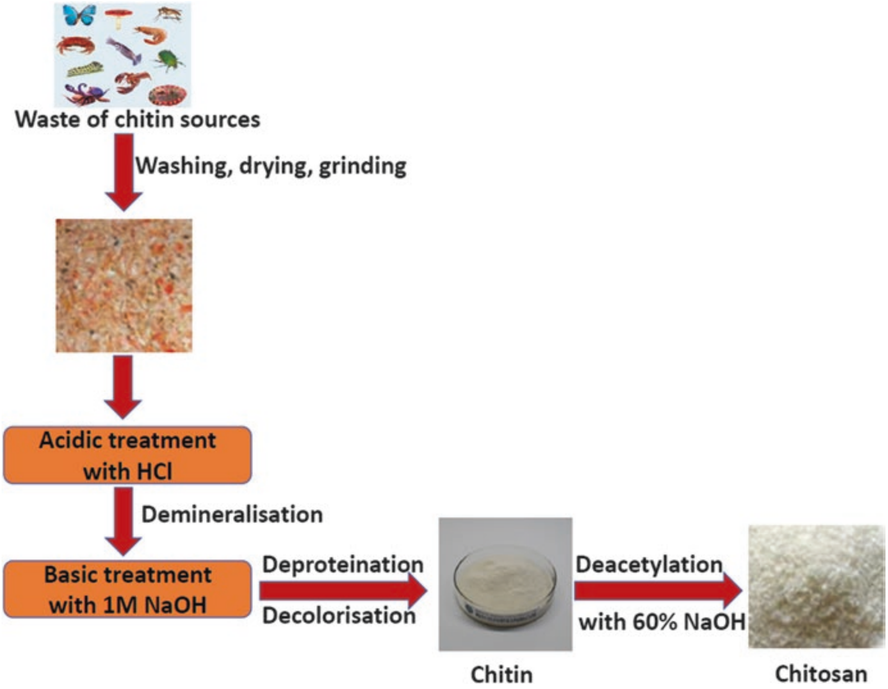


Fig. 11.7 Extraction of chitosan

Chitosan is a non-toxic, biodegradable, biocompatible and nonimmunogenic natural polymer with the existence of modifiable positions in chemical structure and hence has potential to be processed in many forms (Anitha et al. 2014). The chitosan molecule can be modified either by physical modifications or by chemical modifications to beads, films, hydrogels, nanofibers, nanocomposites and nanopowder as shown in Fig. 11.8. Chemical modifications can be achieved either by grafting which involves insertion of functional groups or by crosslinking reactions; bonding the macromolecular chains with each other leads to the formation of chitosan derivatives with superior properties such as increase in adsorption capacity and resistance toward extreme medium conditions.

Different forms of chitosan like film (Salehi et al. 2016), nanofiber (Habiba et al., 2017), powder (Chang et al. 2006) and beads (Lazaridis and Keenan 2010) were obtained through various physical modifications. Recently, chitosan-based composites have been reported which not only overcome the drawbacks of chitosan but also offer physical strength and magnetism (Golie and Upadhyayula 2017; Liu et al. 2015).

In recent years, scientists have focused their attention on development of chitosan nanofibers with customizable pore sizes and rationally high specific surface areas (Li et al. 2013a; Huang et al. 2015). Min et al. 2015 synthesized pure chitosan electrospun nanofiber membranes (average diameter ~ 129 nm) to remove As (V) from water. Habiba et al. (2017) have used blending and electrospinning methods for the production of chitosan/(polyvinyl alcohol)/zeolite composite nanofibers.

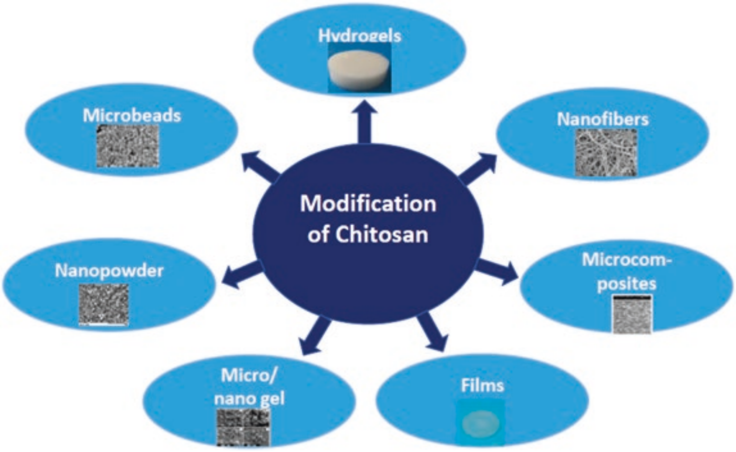


Fig. 11.8 Different forms of chitosan used in wastewater treatment

These composite nanofibers have shown good stability in solutions at different pH and with recycling up to five runs. Various chitosan derivatives with good adsorption capacity together with good mechanical resistance and chemical stability could be synthesized via chemical modification.

Chemical modification can be achieved through different kinds of reactions such as esterification, xanthation, oxidation (Zhu et al. 2012; Chen and Wang 2012), acylation (Repo et al. 2013; Guo et al. 2016), etherification (Viswanathan et al. 2009; Ge and Luo 2005), Schiff base reaction (Tanhaei et al. 2015; Elwakeel et al. 2017), phosphonium enhancement (Sessarego et al. 2019) and alkylation (Qin et al. 2003; Cárdenas et al. 2001). Numerous studies have clearly demonstrated the outstanding coagulation and flocculation properties of chitosan for dye molecules in textile wastewater (Szyguła et al. 2009), heavy metals and phenolic molecules in cardboard-mill wastewater (Renault et al. 2009b) organic matter in pulp and paper mill wastewater (Rodrigues et al. 2008) and inorganic suspensions in kaolinite suspension (Li et al. 2013b). This wide range of application clearly demonstrates the potential of chitosan and chitosan derivatives for water and wastewater treatment.

11.5.2 Cellulose

Cellulose is a long linear chain polymer of β-D-glucopyranose repeat units linked together by β-1,4-glycosidic linkage (Fig. 11.9). It is one of the most abundant natural polysaccharides among all the polymers present on earth and derived from different wood sources as shown in Fig. 11.10. The characteristic property of chirality, hydrophilicity or hydrophobicity and degradability of cellulose largely depends on its molecular structure. As pure cellulose has very limited applications, in recent years, serious efforts have been taken to modify its properties by improving its physical and chemical structure which broaden its industrial applications (Das et al. 2012).

Fig. 11.9 Cellulose-β-1,4-linkage

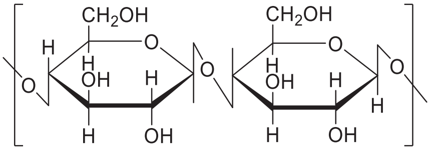
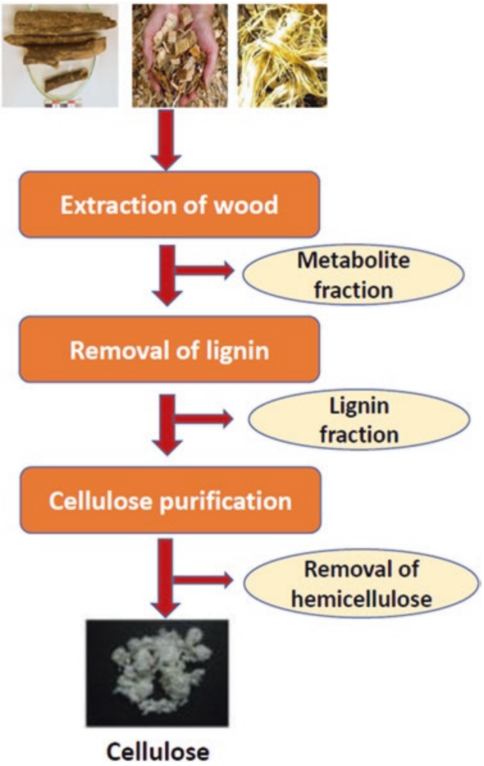


Fig. 11.10 Extraction of cellulose from wood sources



There are two main approaches for the conversion of cellulose into its derivatives. The first approach involves a direct introduction of chelating or metal binding functionalities into the cellulose backbone (Saravanan and Ravikumar 2015) whereas alternative approach involves grafting of selected monomers to the cellulose backbone (Aoki et al. 1999; Singh and Guleria 2014; Kumar et al. 2019b). Such kind of chemical modifications not only increases the adsorption capacity of cellulose derivatives for heavy metals in aqueous and nonaqueous media (Kamel et al. 2006) but also used to vary several other properties of cellulose, such as absorptivity, hydrophobicity or hydrophilicity, elasticity and microbial, heat and mechanical resistance (McDowall et al. 1984). The most important functionalization processes of cellulose occur through etherification, esterification, oxidation and halogenation (O'Connell et al. 2008).

In another study, Khiari et al. (2010) prepared anionic sodium carboxymethylcellulose from agricultural waste, i.e. date palm rachis coupled with aluminium sulphate as coagulant, and tested it as eco-friendly flocculants for removal of turbidity in drinking water treatment. Recently, Suopajärvi et al. (2013) have reported anionized nanocellulose flocculant with ferric sulphate coagulant and examined its flocculating properties in municipal wastewater.

11.5.3 Alginates

In 1881, alginate was first isolated by Stanford (1881). Alginate is present as sodium, magnesium and calcium salts of alginic acid in different species of brown seaweed (Phaeophyceae). Therefore, commercial alginates are extracted from *M. pyrifera*, *S. japonica*, *A. nodosum* and *L. hyperborea* (Gomez et al. 2009). In addition to seaweed origins, bacterial origin alginates are also reported; however, such kind of alginate is not yet commercially available (Mærk 2014). The process of extraction of alginate has been well documented in the literature and is relatively straightforward as shown in Fig. 11.11 (Smith and Miri 2010).

Alginate is a heteropolysaccharide of two uronic acid monomers, i.e. 1→4-linked β-ᴅ-mannuronic (MA) and 1→4-linked α-l-guluronic acid (GA) (Fig. 11.12). These residues are arranged randomly throughout the polysaccharide chain providing irregular geometry which impacts the packing ability of the polymeric chains. Such arrangements have significant impact on the physical properties of alginate. In general, large proportion of G blocks provides stiffer conformation and large proportion of M blocks provides more flexible conformation to corresponding alginates. The abundance of various functional groups such as hydroxyl, carboxylic and oxo groups gives alginic acid/salts strong chelating properties for metal ions.

Various chemical treatments such as phosphorylation, carboxylation and sulfonation may be applied on alginic acid in order to increase metal uptake capacity (Jeon et al. 2002); however, such treatments tend to increase the cost of the final product. A recent study investigated flocculating efficiency of sodium alginate in synthetic dye wastewater and in treatment of industrial textile wastewater by using aluminium sulphate as coagulant (Wu et al. 2012). Alginate derivatives were also studied for their capacity to adsorb different metals as shown in Table 11.1 and hence have a significant role in wastewater treatment.

11.5.4 Gum and Mucilage

Gums and mucilage have been emerged as a safer alternative to traditional polymers in wastewater treatment because their production and applications are environment-friendly and advantageous to human as well as for our ecosystem. Several natural adsorbents and flocculants based on gums and mucilage are derived from various

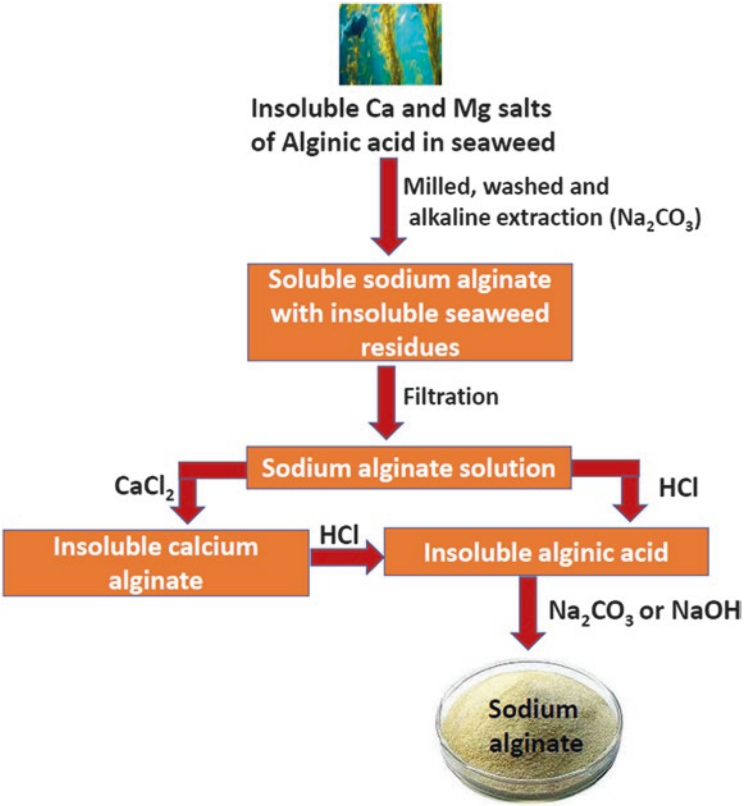


Fig. 11.11 Extraction of alginic acid from seaweed

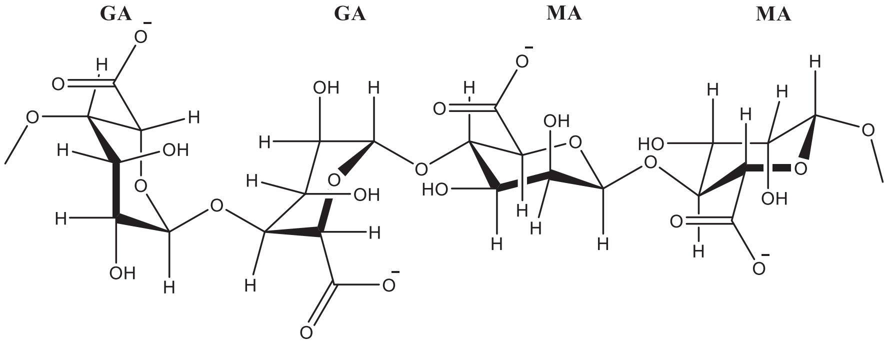


Fig. 11.12 Structure of alginate with repeat units of gluconic acid (GA) and mannuronic acid (MA)

Table 11.1 Metal sorption studies on alginate-based products

References	Adsorbent	Metals
Jeon et al. (2005)	Carboxylated alginic acid	Cu (II), Pb (II)
Karagunduz et al. (2006)	Dried alginate beads	Cu (II)
Al-Rub et al. (2004)	Alginate beads	Ni (II)
Papageorgiou et al. (2006)	Alginate beads	Cu (II), Cd (II), Pb (II)
Park and Chae (2004)	Alginate beads, alginate capsules, alginate gel coated	Pb (II)
Ablouh et al. (2019)	Chitosan microspheres/sodium alginate hybrid beads	Pb (II), Cr (VI)

plant species including *P. psyllium* (psyllium), *P. ovata* (isabgol), *T. foenum-graecum* (fenugreek), *H. esculentus* (okra), *T. indica* (tamarind) and *M. sylvestris* (mallow) and have shown promising results with regard to the treatment of textile wastewater (Mishra and Bajpai 2005), landfill leachate (Al-Hamadani et al. 2011), biological effluent (Anastasakis et al. 2009), sewage effluent (Mishra et al. 2003) and tannery effluent (Mishra et al. 2004).

In some cases, their effectiveness was comparable to synthetic flocculants in terms of treatment efficiency even at low concentrations. Agarwal et al. (2001) and Mishra et al. (2004) have developed bio-flocculants from okra gum and fenugreek mucilage, respectively, and tested them for sewage wastewater and tannery effluent and found that the flocculation efficiency of these was at par with synthetic polyacrylamide. In general, these plant-based adsorbents/flocculants are obtained by aqueous extraction, filtration, precipitation with alcohol and drying as shown in Fig. 11.13.

Gum xanthan-psyllium-cl-poly(acrylic acid-co-itaconic acid)-based adsorbent has been synthesized and screened for effective removal of cationic and anionic dyes from the aqueous fluid. The adsorbent exhibited good removal and recyclability efficiency for the dyes auramine O (Aur-O) and eriochrome black T (EBT) with minimal activity decline after six and three cycles, respectively (Chaudhary et al. 2018). Most recently, binary grafted psyllium (Psy-g-Poly) was synthesized and tested for removal of Hg (II) ions from aqueous solution. The adsorbent exhibited high adsorption efficiency of about 96% at 100 ppm concentration of Hg (II) ions (Kumar et al. 2019a).

11.5.5 Tannin

Tannin is an anionic polymer (Özacar and Şengil 2000) obtained from vegetal secondary metabolites such as fruits, bark, leaves and others (Beltrán Heredia and Sánchez Martín 2009a, b) and biodegradable in nature. Its potential for wastewater treatment has been tested by removal of suspended pollutants from synthetic raw water (Özacar and Şengil 2000), removal of suspended and colloidal matter present in drinking water (Özacar and Şengil 2003) and removal of ink, pigments and dyes

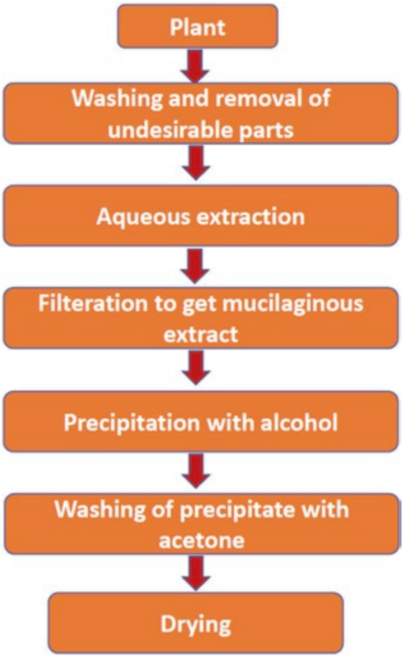


Fig. 11.13 Processing steps for biopolymers from gum and mucilage

from ink-containing wastewater (Roussy et al. 2005). In all these studies, anionic tannin flocculated the destabilized colloidal particles by bridging and tucked them together to form flocs of large size which undergo sedimentation.

Modified tannin (Tanfloc) is obtained from the bark of *Acacia mearnsii* and further modified by a physico-chemical process is used to remove heavy metals from polluted surface water and in municipal wastewater treatment (Beltrán Heredia and Sánchez Martín 2009b). Chemical modification such as addition of hydrocolloid gums, soluble salts and generation of quaternary nitrogen to give Tanfloc cationic character makes it capable to directly use in wastewater treatment. New adsorbent poly(tannin-hexamethylendiamine) (PTHA) was developed by varying mole ratio of tannin and hexamethylendiamine under one-pot green synthesis method and used for Cr (VI) removal from aqueous solution (Liu et al. 2018). Most recently, tannin-supported on cellulose (TM) microfibers were successfully synthesized to remove cationic dye in aqueous solution (Wang et al. 2019).

11.6 Advantages and Current Challenges

With great awareness of potential harms caused by chemical and synthetic adsorbent and flocculants, most of the countries have started to strictly control its usage in drinking water and wastewater treatment. Researches are going on to replace the conventional flocculants by highly efficient and eco-friendly bio-adsorbent and flocculants. The biodegradability, non-toxicity, cost-effectiveness and easy availability from reproducible agricultural resources have attracted wide interest from researchers towards biopolymers for the development of new generation adsorbent and flocculants.

Several biopolymers such as alginates, starch, cellulose, chitosan, tannin, gums and mucilage have been investigated for their adsorbing and flocculating properties in wastewater treatment and they exhibit excellent selectivity towards toxic compounds and metals, thus efficient in the removal of pollutants from wastewater. However, it was reported that their applicability and feasibility is restricted by moderate absorbing and flocculating properties and short shelf life. This problem is addressed by developing modified biopolymers either by crosslinking or by grafting and such modified biopolymers are claimed to have remarkable pollutant removal properties and biodegradability.

There are several factors that constraint the development and application of modified biopolymers to pilot scale or in other industries such as chemicals used in the synthesis process of biopolymers may cause health and safety issues, complexity of synthesis process and requirement of high energy input for production of larger quantities and relatively high equipment cost for the synthesis restrict its application. In order to address all these challenges, exhaustive investigation is required to prove the validity of modified biopolymers and promote their industrial applications. More research is urgently required to derive maximum benefits of grafting and crosslinking technology and modified biopolymers in order to balance the high cost of scaling up and operation.

11.7 Conclusion

Due to the increasing demand of environment-friendly technologies for turbidity and contaminants, removal represents an important progress in sustainable environmental technology. Biopolymers are nontoxic, biodegradable and cheap and can be obtained from renewable resources and their application is directly related to the improvement of quality of life. Modification of biopolymers with chemical crosslinking and grafting has been studied recently to improve its characteristics. Several studies have been conducted to investigate the adsorbing or flocculating properties of biopolymers in wastewater treatment. The results verified that they are technically promising adsorbents and flocculants with high removal efficiency of toxic pollutants. All the studies of modified biopolymers took place under lab-scale conditions and their applications at industrial scale are still at their early stages. Therefore, for the sake of environment and human health, more qualitative and quantitative researches are required to be carried out to further exploit the potential of biopolymers in drinking and wastewater treatment plant.

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Chapter 12
Recovery of Rare Earths, Precious Metals and Bioreduction of Toxic Metals from Wastewater Using Algae

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Abstract For many decades, toxicity of metals has been recognised due to documented evidence in plants, animals, water and/or humans. Unlike toxic heavy metals which are relatively abundant, some metals are scarce and unevenly distributed in the earth crust. Rare earth elements (REE) are ranked as one of the most critical elements with a diminishing supply. In addition some heavy metals such as thallium are rare but widely distributed in very low concentration and listed under critical metals comparable to cadmium and lead. Advanced and cleaner technologies using biological materials serve as an efficient and complementary treatment method for dissolved toxic metals and recovery of precious and REE. Various living and dead organisms have been investigated for metal removal, e.g. bacteria, fungi, algae, yeast and industrial and agricultural waste. Phytoremediation using higher plant accumulators has been widely embraced for ecosystem restoration especially for long period of time. This can eventually promote industrial environmental sustainability and restore ecosystem functioning. Bio-adsorption technologies using dead organisms offer the opportunity for recycling in addition to being eco-friendly. The challenge is to select the most efficient biosorbents from the relatively abundant biomass. This chapter, therefore, provides an insight into the various bioremediation technologies currently being explored from our research group for microalgae for the treatment of heavy metals such as cadmium, thallium and chromium. In addition, recovery of precious and rare earth elements such as gold and lanthanum using various eluents is also discussed. Some of the challenges and way forward are highlighted in the conclusion.

Keywords Rare earths · Precious metals · Recovery · Bioreduction · Wastewater · Algae

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12.1 Background

Toxicology of metallic species has been investigated broadly due to its adverse negative impacts along the food chain since they cannot be degraded, hence causing irreversible health effects to biota (Gupta and Rastogi 2008; Chojnacka 2010; Bilai et al. 2018; Saxena et al. 2019a, b). Metals are vital in the environmental functioning and ecosystem health. However, metals become toxic when the threshold of environmental adaptive capacity is exceeded. For instance, numerous authors have noted that human physical complications are attributed to deficiency and toxicity of metals (Yu 2008; Bharagava et al. 2008; Yaylal-Abanuz 2011; Brevick and Burgess 2013; Kalumba 2016). With advances in technology and increased demand of metal utilisation in industrial development, point source pollution is the main contributor to environmental degradation of water resources (Shukla et al. 2018; Saxena et al. 2019a, b).

Metals are propelled by natural and anthropogenic processes into the environment through corrosion, atmospheric dispersions and deposition, soil erosion, leaching, weathering and volcanic eruption, industrial and domestic waste disposals and fertiliser application (Tchounwou et al. 2012; Bharagava et al. 2018; Kishor et al. 2019), among others. Consequently, environmental metal mobility and availability depends on many chemical and biochemical processes such as precipitation-dissociation, adsorption-desorption, complexation-dissociation and oxidation reduction (Prasad and Hagemeyer 1999; Kalumba 2016).

Unlike toxic heavy metals which are relatively abundant, some metals are scarce and unevenly distributed in the earth crust. Rare earth elements (REE) are ranked as one of the most critical elements with many emerging technologies but with a diminishing supply (European Commission 2010; Bharagava et al. 2014). The growing demand for precious metals in industrial and medical applications has exerted pressure on the limited natural resources. Therefore, recovery from secondary sources is a renewable way to protect an irreplaceable resource that otherwise would be discarded (Izatt et al. 2014).

Traditional technologies such as advanced oxidation, chemical precipitation, membrane processes, ion exchange and adsorption have been used in the treatment of organic/inorganic materials. These technologies have high energy requirements, input chemicals and generate secondary waste, hence rendering them inefficient for treatment of high volume of wastewater containing low metal concentrations (<100 mg/L) (Ahluwalia and Goyal 2007; Hansda and Kumar 2016). So far, adsorption is the most effective in advanced wastewater treatment (Reddy and Lee 2012; Anastopoulos and Kyzas 2016). Many commercial adsorbents including activated alumina, zeolites and silica gel have been used for the treatment of heavy metals (Bhatnagar and Sillanpaa 2010). These adsorbents have better adsorption properties due to a high surface area but are generally costly and non-biodegradable.

This attracted the use of biodegradable activated carbon, which is found to be highly efficient due to the high porosity and large surface area but also very costly (Babel and Kurniawan 2004; Fu and Wang 2011). Advanced and cleaner technologies using biological materials act as an efficient and complementary treatment method for dissolved toxic metals and recovery of precious and rare earths (Bilai et al. 2018). These technologies offer a relatively lower cost due to absence of creation of secondary problems, environmentally friendly and potential for reusability of biomass.

12.2 Toxicity of Heavy Metals

Heavy metals are classified according to their chemistry coordination, a factor determined by the element's electron environment (Ferris 1989; Collins and Stotzky 1989). The United States Environmental Protection Agency (US EPA) has listed priority metallic pollutants such as mercury, lead, cadmium, thallium, zinc, copper, nickel, beryllium and antimony. The list also includes transitional metals such as chromium and metalloids such as arsenic and selenium. Even metals such as iron, zinc, molybdenum and magnesium which are essential nutritional supplements to plants and animals can become toxic to the organisms when discharged in excess (Hughes and Poole 1991). Some heavy metals are described below in detail of toxicity levels and effects to public health and the environment.

12.2.1 Thallium Toxicity

In nature, thallium (Tl) minerals are rare but widely distributed in very low concentration (Xiao et al. 2012) as indicated in Table 12.1. Thallium (III) toxicity is considered to be higher than cadmium (Cd II) as the bioavailability of the former is much lower to hydrolysis and stability constants (Ralph and Twiss 2002; Twining et al. 2003). Earlier studies suggested that Tl (I) forms soluble compounds with, e.g. sulphates, acetate and carbonates and is more abundant than Tl (III) (Goldschmidt 1954; Galván-Arzate and Santamaría 1998).

Table 12.1 Mean abundance of thallium distribution in natural environment

Distribution in nature	Mean abundance	References
Earth's upper crust	0.75 mg/kg	Taylor and Mclennan (1985)
Sedimentary rocks	0.27–0.48 mg/kg	Heinrichs et al. (1980)
Groundwater	0.001–0.25 μg/L	Frengstad et al. (2000)
Metamorphic rocks	0.65 mg/kg	Heinrichs et al. (1980)
Seawater	0.012–0.016 μg/L	Flegal and Patterson (1985)
Lake water	0.001–0.036 μg/L	Lin and Nriagu (1999)
Shales and schists	0.5–2.0 mg/kg	Kazantzis (2000)
Acidic rocks	0.5–1.8 mg/kg	Kabata-Pendias and Pendias (2001)
Igneous rocks	0.06–1.2 mg/kg	De Albuquerque and Shaw (1972)

Thallium has a low boiling point and easily volatilises as an impurity from coal combustion, smelting operations, cement industry, steel industry, sulphuric acid production, auto-emissions and refining processes (Jacobson et al. 2005; Vaněk et al. 2011; Tatsi et al. 2015). Various Tl compounds are also used as catalysts in the oxidation, reduction, aromatisation, esterification and polymerisation of organic molecules (Nriagu 1998). Industrial emissions are approximately 2000–5000 tons per year in vapours, dust, fluids and solids (Karbowska et al. 2014). Due to the similarity of Tl (I) and potassium (K (I), Tl (I) disrupts functioning of several enzymes as it enters the transport system inhibiting K (I) movement across mitochondrial membrane (Leonard and Gerber 1997; Repetto et al. 1998).

Thallium poisoning in humans mainly occurs through ingestion of contaminated food, through inhalation and/or through the skin. Depending on the type of exposure, dosage and age, it may be acute, subacute or chronic (Mulkey and Oehme 1993). The negative effects of exposure include encephalopathy; tachycardia; mild gastrointestinal disturbances; degenerative changes in kidney, liver and heart; alteration of nervous system; and eventually death (Cavanagh et al. 1974; Nriagu 1998; Urík et al. 2010). Effects of chronic exposure to low concentrations are not well known (Karbowska 2016), but bioaccumulation is lethal especially to humans. The permissible threshold limits for Tl have been set by the Environmental Protection Agency (US EPA 1980) at 0.002 mg/L for drinking water and 10 $\mu g/m^3$ for air content.

12.2.2 *Cadmium Toxicity*

Cadmium is a silvery white lustrous heavy metal with a relatively high vapour pressure. This metal has eight stable isotopes with the most common ones being ^{112}Cd and ^{114}Cd (Adriano 2001). Cadmium is widely used in industrial applications such electroplating of steel, iron, copper, etc., in manufacture of electrode batteries and as an additive in the making of pigments. Cadmium is also found in phosphate fertilisers, stabilisers, alloys, barrier for atomic fission control, ceramics, plastics, paints, coated fabric, printing ink rubber and glass enamel (Förstner 1980; Balkaya and Cesur 2008; Cobb 2008). Cadmium forms soluble salts of arsenates, phosphates, carbonates and ferrocyanide (Rahimzadeh et al. 2017). Several literature sources have provided commentary on cadmium toxicity (Waalkes et al. 1992; Waalkes 2003; Huff et al. 2007). Cadmium replaces essential elements like Zn, Ca and Fe causing displacement from proteins (Verbruggen et al. 2009).

Cadmium exposure causes skeletal demineralisation with the most severe form being "itai-itai" disease (Murata et al. 1970; Friberg et al. 1974; Yasuda et al. 1995; Umemura and Wako 2006). Acute poisoning usually occurs in the lungs and gastrointestinal tract causing health effects such as bronchitis, pneumonitis and toxemia in the liver, vertigo, diarrhoea and abdominal pain (Friberg et al. 1974; Tsuchiya 1981). Chronic effects of Cd poisoning usually accumulate in the lungs, kidney and bones. Long-term exposure distends air sacs reducing lung capacity; kidney damage produces proteinuria, aminoaciduria, phosphaturia, glucosuria, and kidney stones. Other health risks of cadmium include hypertension, testicular atrophy, kidney failure, cancer, mucous membrane destruction, anaemia, osteomalacia in bones and reproductive toxicity (Fleischer et al. 1974; Leyva-Ramos et al. 1997; Godt et al. 2006).

Some of the treatment methods traditionally used for removal of cadmium from wastewater include precipitation of metals as insoluble hydroxides, carbonates or sulphides (Karthikeyan et al. 1996; Lin et al. 2005); cementation with zinc powder (Ku et al. 2002); membrane processes such as hollow fibre, supported liquid membrane and emulsion liquid membrane (Mortaheb et al. 2009); and liquid-liquid solvent extraction using specific extractants (Gupta et al. 2001). Ion exchange using resins has also been investigated widely for Cd removal by different authors (Chen et al. 1998; Malla et al. 2002; Pehlivan and Altun 2006). The permissible limits of cadmium discharge in wastewater and drinking water are 0.1 and 0.05 mg/L, respectively, according the World Health Organisation (WHO 2011).

12.2.3 Chromium Toxicity

Chromium is a transitional metal that occurs in various oxidation states, mainly hexavalent chromium [Cr(VI)] or trivalent chromium [Cr(III)] (Saha et al. 2011). Cr(VI) is considered much more toxic than Cr(III) (Miretzky and Cirelli 2010; Bharagava et al. 2018). Cr is very functional and has desirable properties which lead to a wide variety of uses such as stainless steel and non-iron alloy production, metal plating, leather tanning, textile preservatives, printing and dying and development of pigments and in refractories (Guertin et al. 2016). The Cr(VI) compounds such as chromate ion (CrO_4^{2-}) contaminate soil, sediment, surface waters and groundwater and can enter living organisms through numerous receptor pathways (Szulczewski et al. 1997).

The $HCrO_4^{2-}$ form exists if the pH of the solution is greater than 7, while in the pH between 1 and 6, CrO_4^{2-} is predominant. Therefore, within the normal pH range in natural surface waters, CrO_4^{2-} and $Cr_2O_7^{2-}$ ions are expected to occur which are quite soluble and mobile in water streams (El Nemr et al. 2015). The structural similarity of CrO_4^{2-} with phosphate ion (PO_4^{3-}) and sulphate ion (SO_4^{2-}) allows Cr(VI) to be readily transported across biological membranes and into cells (Gutiérrez-Corona et al. 2016). Once Cr(VI) is in the cells Cr(VI) generates active Cr(V) and/or Cr(IV) intermediates, free radicals and Cr(III) as the final product. The Cr(III) inside the cell interferes with DNA replication and causes mutagenesis (Xu et al. 1996). Ingestion of Cr(VI) compounds results in severe gastrointestinal disorders, haemorrhagic diathesis, convulsions and ultimately death (Baruthio 1992).

Chemical reduction and precipitation is one of the main remediation treatments available for chromate-contaminated industrial wastewater. Cr(VI) is chemically reduced to Cr(III), the less toxic form, under acid conditions. Iron(II) chloride or iron(II) sulphate is typically used as the electron donor for the reduction reaction which can produce solid waste such as ferric hydroxide (Jardine et al. 1999). Following the reduction reaction an alkali such as sodium hydroxide or calcium hydroxide slurry is used to neutralise the acidity and precipitates the Cr(III) (Barrera-Díaz et al. 2012).

Electrochemical reduction is also used to treat Cr (VI) contamination. Two electrodes are used, namely, a cathode and an anode. At high current systems Cr (VI) is reduced directly at the cathode and at low current systems the Cr (VI) is converted to Cr (III) through reduction by Fe(II) forms. At this pH range the Fe (II) ions form an insoluble species onto which the Cr (III) ions are absorbed (Mukhopadhyay et al. 2007). At low pH, electro-dissolution of Fe electrodes involves ionisation of Fe which reacts directly with the Cr (VI) in the solution reducing it to Cr(III) (Barrera-Díaz et al. 2012).

Adsorption processes can remove Cr contamination under the right conditions. Activated carbon is a well-established adsorbent for removing organics and metals from solutions. Adsorption of Cr(VI) to activated carbon is primarily due to electrostatic attraction and this process depends on the pH of the solution. Conducting polymers such as polypyrrole (PPy) and polyaniline (PANI) have been shown to be cost-effective adsorbents for Cr(VI) removal due to their ion exchange properties and inherent ability to reduce Cr(VI) to less toxic Cr(III). The adsorption-coupled reduction reaction is considered the main mechanism of Cr(VI) adsorption under acidic conditions.

Many studies have found that anionic Cr(VI) species (CrO_4^{2-} and $HCrO_4^-$) is adsorbed onto positively charged surfaces/adsorbent at low pH values. Under acidic conditions the potential for Cr(VI) to be reduced to Cr(III) is increased (Miretzky and Cirelli 2010). Various adsorbents have been used for treating Cr(VI) containing water including activated carbons, zeolites, biosorbents, clay minerals and oxides, polymeric resins and agricultural and industrial waste materials (Miretzky and Cirelli 2010). The drawback of adsorption processes is the chemical addition as a pretreatment to lower pH (Kera et al. 2017).

12.3 Precious Metals and Rare Earth Elements

12.3.1 Gold

Due to its excellent thermal and electrical conductivity and high corrosion resistance, gold is indispensable in electronics for semiconductors and connectors in computer technology. It is also used in jewellery, dental work, electrical contacts and wires, photography and as a coloured coating for special types of glass. Gold is also good at reflecting heat and thus often used as the plating on spacecraft to keep them cool. Different species of gold have been applied in medicine; e.g. a radioactive isotope of gold (198Au) and a compound of gold (sodium aurothiomalate) are often used to treat cancer and rheumatoid arthritis, respectively (Izatt et al. 2014).

Therefore, with the growing demand of its industrial and medical applications and its limited natural sources, recovery of gold from secondary sources, such as the waste electrical, printed circuit board, spent electroplating wastewater and other solutions, is an alternative to recycle an irreplaceable resource that otherwise would be discarded (Izatt et al. 2014).

Hydrometallurgy can be directly applied in recovery of liquid gold sources, but in case of solid gold sources, the procedure leaching is needed prior to hydrometallurgy by using suitable lixiviants to extract a soluble constituent from a solid substance. Sodium cyanide and potassium cyanide are the most common gold lixiviants to dissolve gold under aerated conditions (Bisceglie et al. 2017). Gold cyanidation is an electrochemical process where the gold dissolves in the alkaline cyanide solution and forms the water-soluble dicyanoaurate (I) gold complex as shown in Eq. (12.1):

$$4\mathrm{Au} + 8\mathrm{KCN} + \mathrm{O_2} + 2\mathrm{H_2O} \rightarrow 4\mathrm{K}\left[\mathrm{Au}\left(\mathrm{CN}\right)_2\right] + 4\mathrm{KOH} \tag{12.1}$$

Due to the toxicity issues of cyanide and the limitation of slow dissolution process, some alternative lixiviants such as thiosulfate, thiourea and halides are developed and applied. For example, the hot aqua regia, a mixture of nitric acid and hydrochloric acid containing chlorine gas (Cl_2/HCl), is widely adopted in small and medium operations (Eq. 12.2), despite the main inconvenience of the production of toxic gas, a major hazard for workplace environments (Mack et al. 2007; Won et al. 2014):

$$2\mathrm{Au} + 3\mathrm{Cl_2} + 2\mathrm{HCl} \rightarrow 2\mathrm{HAuCl_4} \tag{12.2}$$

Thiourea ($CS(NH)_2$) has received considerable interest as an alternative lixiviant for gold extraction with several advantages over the conventional cyanidation (Ubaldini et al. 1998), such as a low environmental impact, an easier handling of reagent, a greater selectivity towards gold and fast kinetics of gold dissolution. In the presence of a suitable oxidising agent, such as O_2, H_2O_2 or Fe^{3+}, thiourea will solubilise gold to give a gold(I) species (Eq. 12.3):

$$\mathrm{Au} + 2\mathrm{CS}\left(\mathrm{NH_2}\right)_2 \rightarrow \mathrm{Au}\left[\mathrm{CS}\left(\mathrm{NH_2}\right)_2\right]^{2+} + \mathrm{e} \tag{12.3}$$

However, with the main disadvantages of expensive oxidant ferric ion, higher consumption of reagent in comparison with cyanide and several technical problems associated with the use of thiourea, few industrial applications have been achieved to date.

In hydrometallurgical process, chemical precipitation, solvent extraction and ion exchange are the most extensively employed methods to recover the gold from those leaching aqueous solution. Various other methods such as zinc dust cementation and activated carbon adsorption have also been applied for the recovery of gold and other precious metals (Ju et al. 2016). Some modified activated adsorbents act as an alternative to commercial activated carbon for gold recovery, which are generated from agriculture and industrial by-products such as eggshell membrane, dealginated seaweed, alginated beads and persimmon tannin (Maruyama et al. 2014; Ju et al. 2016). However, the main limitations of these methods shown in Table 12.2 have restricted their application in recovery of gold from wastewaters. This has motivated researchers to develop alternative technologies for separation, pre-concentration and removal of gold ions from aqueous solutions especially for the treatment of low concentration metal wastewater (below 10–40 mg/L) (Ju et al. 2016).

12.3.2 Lanthanum

Lanthanum is one of the most abundant and commonly used rare earth metals (REE) in industrial processes. Rare earth elements (REE) are a group of metals constituting 17 elements of which 15 are lanthanides. These metals can be grouped into light rare earth metals, lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium

Table 12.2 Advantages and disadvantages of conventional and current technologies for gold recovery

Technologies	Advantages	Disadvantages	References
Chemical precipitation	Simple and cheap operation means	Large volume of wastewater to be treated, poor selectivity for precipitation steps, lengthy refining time and labour-intensive processes	Won et al. (2014), Mack et al. (2007)
Solvent extraction	High selectivity, short operation times, high purity	Solvent loss and subsequent wastewater treatment	Mooiman and Miller (1991), Parajuli et al. (2006)
Ion exchange	High recovery efficiency	Pretreatment required, limited availability of highly selective resins, regeneration of spent resins	Gomes et al. (2001), Kurniawan et al. (2006)
Zinc dust cementation	High recovery efficiency	High initial capital cost, intensive energy consumption and process complexity	Miller et al. (1990)
Activated carbon adsorption	Large surface area and high adsorption capacity	High cost for production and regeneration of activated carbon	Ishikawa et al. (2002), Maruyama et al. (2014)
Biosorption	Low cost, environmentally benign, operation over wide range of pH and temperature, biomass regeneration	Difficulty of separating adsorbents from diluted solutions and lack of selectivity for target metals	Das (2010), Shen et al. (2017)

(Nd) and samarium (Sm), and heavy metals, europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Th), ytterbium (Yb), lutetium (Lu) and yttrium (Y) (Emmanuel et al. 2012). The difference in lanthanides is the electrostatic effect associated with increase in nuclear charge and correlated to the contraction responsible for the weak differences in chemical properties (Martins and Isolani 2005).

This explains the difficulty in separating the elements with several steps involved like solvent extraction and/or ion exchange resins both very costly (Palmieri et al. 2000; Palmieri et al. 2002). Lanthanum is one of the most commonly used REE in industries such as super alloys, special ceramics, catalysts in petroleum refining, motion picture industry for making carbonic lamps, optical industry for making specialised lenses, making of special ceramics and catalysts, among others (Sert et al. 2008; Awwad et al. 2010). The leading producers of REE are China, Australia and the USA with the former having the largest supply estimated at 95% of global production (Binnemans et al. 2013; U.S. Geological Survey 2014). With the increasing economic importance of REE and an increase in supply risk, European Commission (EU 2010) has ranked these metals as critical raw materials (Fig. 12.1) (Binnemans et al. 2013).

Therefore, the need to focus on alternatives for recycling of REE from industrial wastewater and residue containing these metals is required. Recovery of REE from wastewater using conventional methods such as precipitation, extraction and ion exchange is inefficient due to the low concentrations less than 20 mg/L and high concentrations of the associated metals such as titanium, calcium, iron and aluminium (Korenevsky et al. 1998; Chandra et al. 2009; Gaur et al. 2014).

12.4 Bioremediation Technologies

12.4.1 Phytoremediation

Heavy metals break into food chain through biogeochemical cycles from natural leachate, wastes, discharge into the environment and direct application of agrochemicals, grey water use and manure, among others. It can be absorbed by plants from soil with elevated concentration, thus leading to bioaccumulation in plant tissues. Bioaccumulation is a metabolic independent process involving attachment of toxic elements initially at the surface followed by active transportation of metal ions into the cells (Flouty and Estephane 2012; Mishra and Bharagava 2016; Saxena et al. 2019a, b). In bioaccumulation, the tolerance of metal ions is due to the presence of metabolic pathways that utilise toxic metals as a source of energy for growth (Shukla et al. 2018). At a higher concentration of metal ions, it causes phytotoxicity effect, thus inducing oxidative pressure and distorting photosynthetic process which, in effect, deregulate metabolic order in plants (Ibrahim et al. 2011; Gitet et al. 2016; Saxena et al. 2019a, b).

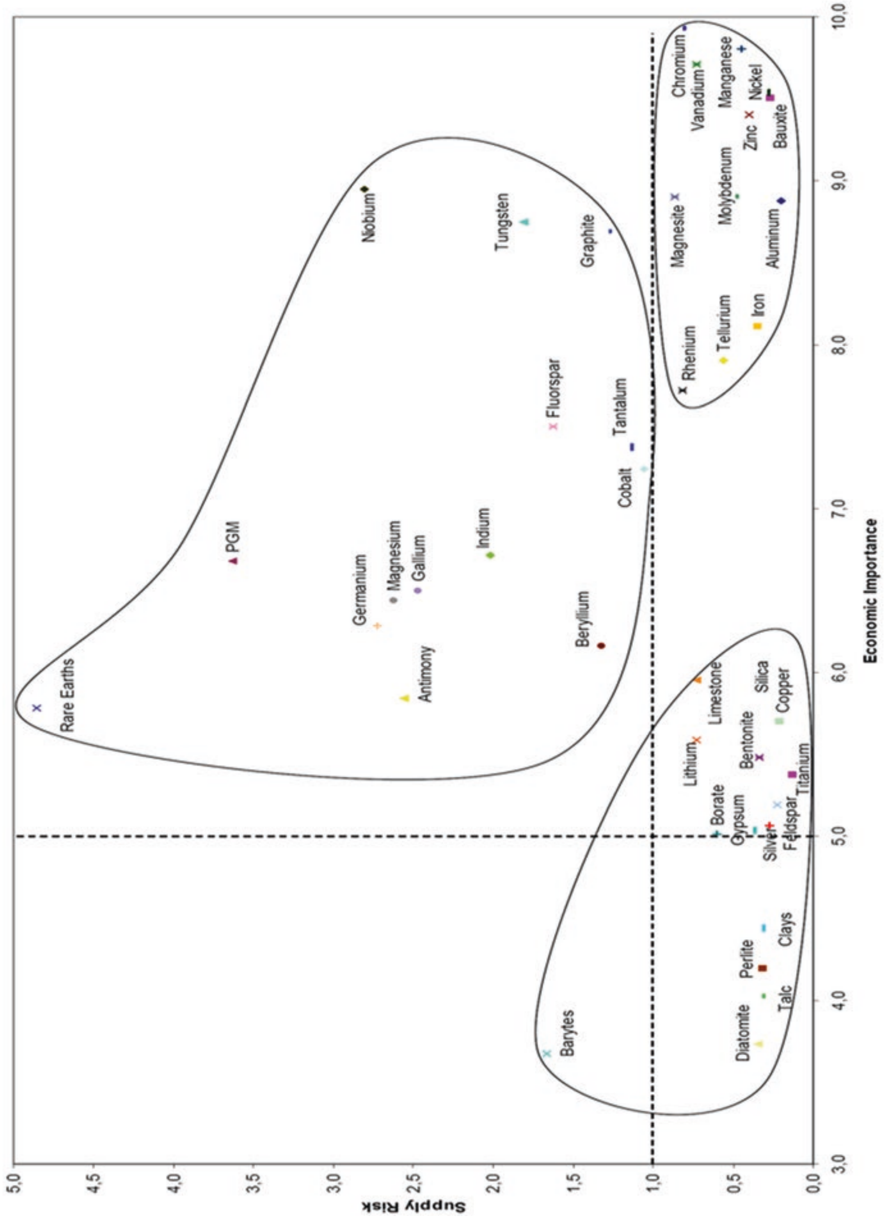

Fig. 12.1 Critical raw materials showing level of supply risk of REE (EU 2010). (Adapted from Binnemans et al. 2013)

Phytoremediation biotechnology, whereby plants are used to clean up the environment, has been widely embraced. Phytoremediation has been defined as the use of green plants and their associated rhizospheric microorganisms, soil amendments and agronomic techniques to remove, degrade or detoxify harmful environmental pollutants (Kadukova and Kavulicova 2010). This offers efficient tools which are environmentally friendly to ecosystem restoration. In addition, the cost of phytoremediation is comparable to regular farming activities (Witters et al. 2009; Kadukova and Kavulicova 2010). Phytoremediation techniques used in environmental cleanup (soil and water) include: phytostabilisation, phytoextraction, rhizofiltration, phytovolatilisation, phototransformation, dendroremediation and hydraulic control, among others (Prasad and Hagemeyer 1999; Kadukova and Kavulicova 2010).

Prasad and Hagemeyer (1999) have noted that the use of plants for remediating trace metal environmental contamination features several merits such as: large-scale application, relative economy, aesthetic value and requiring a smaller reclamation centre for extracting the heavy metals, among others. This would eventually promote industrial environmental sustainability and restore ecosystem functioning. Some plants have been found to be resistant to high metal concentration and can even grow in metal contaminated surroundings (Jobby et al. 2018). These plants can absorb toxic metals from the surrounding soil or hydroponic systems and accumulate the metal inside the plant tissue. These plants are called “hyperaccumulators”. Cr is usually accumulated in the root tissues of plants and is not normally translocated up to aboveground shoots (Lotfy and Mostafa 2014).

The sulphate transport system in the roots allows Cr(VI) to enter the plants. Plants can also neutralise Cr contamination by reducing Cr(VI) to Cr(III), which is then stored in the plant tissue (Cervantes et al. 2001). This ability to reduce Cr(VI) inside the plant is facilitated by specific enzymes which are similar to bacterial chromate reductase. The extent of plant Cr(VI) reduction is difficult to estimate as soils and hydroponic media also reduce Cr(VI) (Cervantes et al. 2001). Cr(III) cations can also be absorbed by plants through a mechanism which include the binding of the positively charged metal ions to negative charges in the cell wall (Lotfy and Mostafa 2014). However, phytoremediation treatment process requires an extended period of time for decontamination of metal in soils (Lotfy and Mostafa 2014). Literature reveals that plants have been central in monitoring metal levels and toxicity in the environment using multiple techniques and methods across the globe. These include FAAS, ICP-AES, ICP, ICP-MS, ICP-OES, CV-AAS, XFS and XRF (Wei and Yang 2010; Su et al. 2014) in different studies.

12.4.2 Bio-adsorption

Bio-adsorption is a passive and metabolically independent process using dead biomass for the treatment of wastewater containing heavy metals (Volesky 1990; Malik 2004). In adsorption, the process occurs at the surface of another molecule while absorption involves incorporation of a substance into another of a different state

(Borda and Sparks 2008; Gaur et al. 2014). The use of dead biomass offers the possibility of regeneration and reuse of the biosorbents, no nutrient requirements, rapid process and pollutant cellular surface bound especially from high volumes of diluted solutions (Volesky 2001; Mehta and Gaur 2005; Chojnacka 2010).

This is mainly attributed to the active functional groups of the cell wall, which provide binding sites, e.g. carboxyl, phosphate, amines, hydroxyl and phenols, among others (Rezaee et al. 2006; Wang and Chen 2009). Figure 12.2 shows the various steps involved in removal and recovery of metals from industrial wastewater using microbial organisms.

12.4.2.1 Mechanisms in Bio-adsorption Processes

There are several mechanisms in the biosorption processes which depend on the type of species and the metal to be sorbed, the binding strength, number of binding sites, functional groups and availability and accessibility of sites (Salama et al. 2017). Due to complexity of solution chemistry, surface composition and structure, some properties operate concurrently to varying degrees (Volesky and Holan 1995; Gaur et al. 2014). Bio-adsorption mechanisms are classified into metabolic dependent and non-metabolic dependent according to their cell functionality (Veglio and Beolchini 1997; Gaur et al. 2014). The metabolic-dependent mechanisms occur in living organisms and involve transport across the cell membrane and precipitation (Brierley 1990; Costa and Leite 1990). The non-metabolic mechanism is different

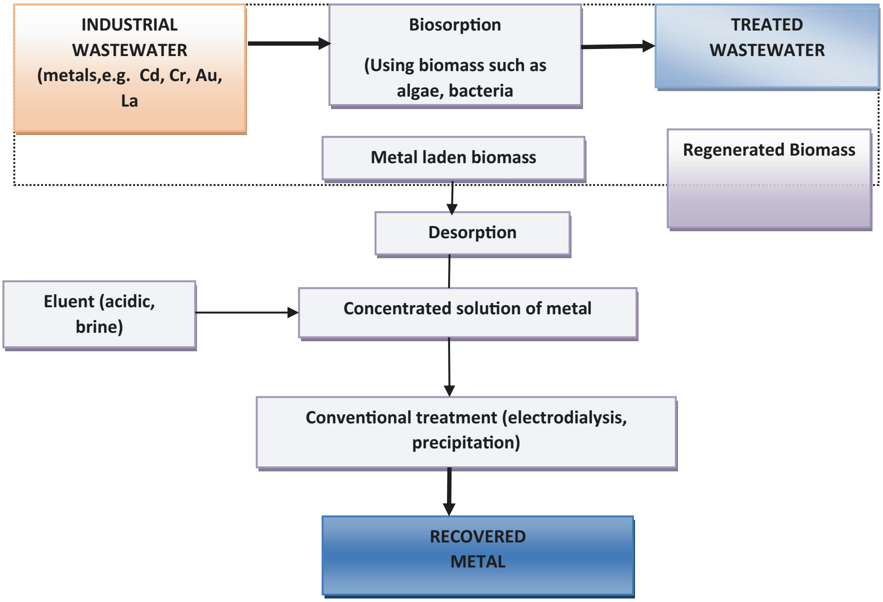

Fig. 12.2 Steps in bio-adsorption and desorption. (Modified from Chojnacka 2010)

on the functional groups on the cell wall and these include ion exchange, coordination, surface precipitation, chelation/complexation and physical adsorption (Farooq et al. 2010; Vijayaraghavan and Yun 2008).

In addition, extracellular polymer substances influence the mechanisms (Li and Yu 2014). A comprehensive understanding of the biosorption mechanisms responsible for metal binding assists in the performance optimisation of new biosorbents. Figure 12.3 shows the various interactions involved in biosorption mechanisms depending on the location of the metal ions either in adsorbate or adsorbent.

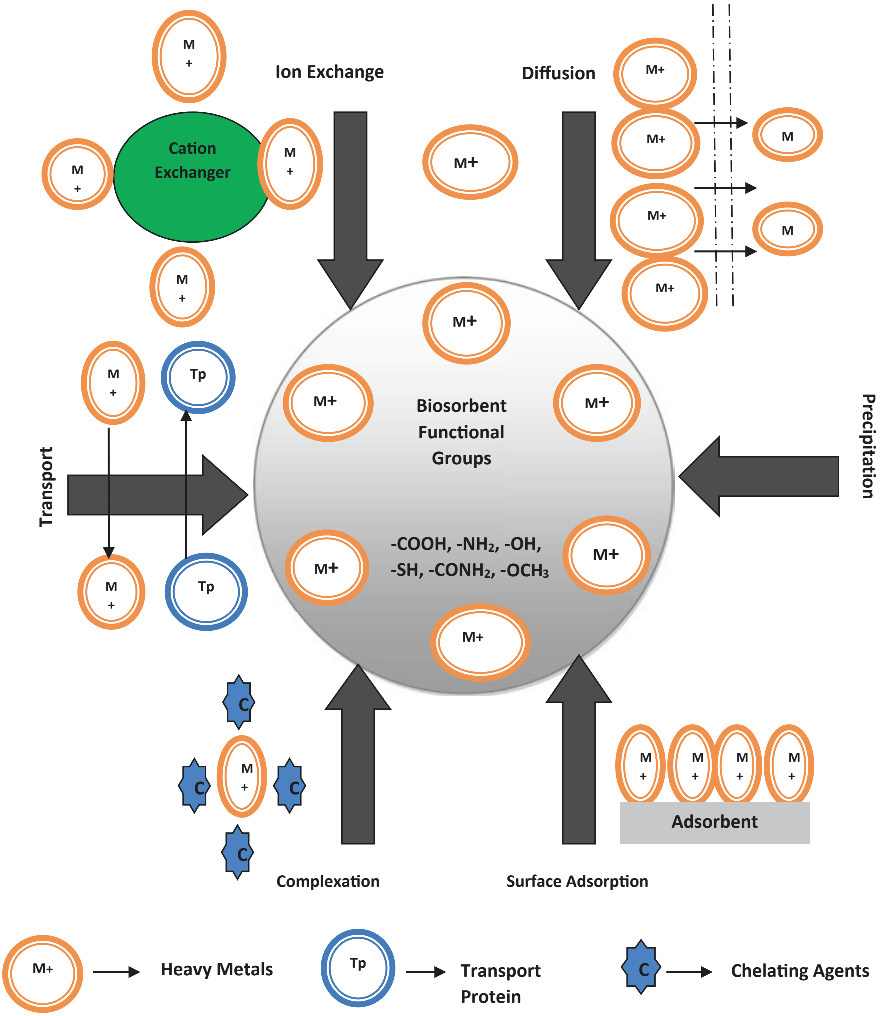

Fig. 12.3 Biosorption mechanism based on cellular metabolism and location of biosorption. (Adapted from Gaur et al. 2014)

Some researchers have reported that ion exchange is the principal mechanism in biosorption (Allen and Brown 1995; Arief et al. 2008; Birungi and Chirwa 2015a). Ion exchange is a reversible chemical where an ion within a solution is replaced by a similarly charged ion attached onto an immobile solid particle (Han et al. 2006). Other researchers suggest an interaction of ion exchange and formation of complexes between metal cations and ligands as well as precipitation of surface of cell wall (Crist et al. 1994; Schiewer and Volesky 2000).

Although several mechanisms have been proposed, the actual mechanisms involved in metal biosorption are not fully understood (Wang and Chen 2006). Analytical techniques can be used to understand possible mechanisms as they complement each other in providing insight of biosorption processes (Park et al. 2010; Michalak et al. 2013). In the biosorption studies using green algae from freshwaters bodies, the algal cell wall was characterised before and after biosorption. It was found that the most active functional groups responsible for lanthanum and thallium sorption included carboxyl, amines and phenols (Birungi and Chirwa 2014; Birungi and Chirwa 2015a).

12.4.2.2 Microalgae as Sorbents for Heavy Metals

Algae are eukaryotic organisms that contain chlorophyll and carry out exogenic photosynthesis. Algal is usually broadly identified under two main groups viz-a-viz macro- and microalgae. Based on their pigmentation, macroalgae are further subdivided into brown seaweed, red seaweed and green seaweed. Microalgae are microscopic organisms with the three most abundant being diatoms, green algae and golden algae (Madigan et al. 1997, Carlsson and Bowles 2007).

Microalgae proliferate everywhere in both freshwater and marine environment and in a range of 200,000–800,000 species with only about 35,000 described (Ebenezer et al. 2012; Cheng and Ogden 2011). In spite of their local availability, only a small percentage of the freshwater algae species that has been investigated thus far has been demonstrated to be capable of adsorbing a wide range of metallic species from wastewater (Davis et al. 2003; Mehta and Gaur 2005; Lesmana et al. 2009).

Many algal studies found that maximum Cr adsorption or loading capacity of the cells increases with an increase in initial Cr ion concentrations (Dönmez and Aksu 2002; Onyancha et al. 2008; Gokhale et al. 2008). This increase is attributed to the increase in the number of ions competing for the available binding sites in the biomass. When the algal cell surface is surrounded by smaller amount of Cr ions, the ions tend to also form multiple bonds with the surface groups; thus the loading capacity gets exhausted even with lower amount of Cr ions adsorbed. At high initial Cr ion concentrations, the ions tend to bind with fewer binding sites (Gokhale et al. 2008). High initial Cr concentration provides an important driving force to overcome mass transfer resistance of metal ion between the aqueous and solid phases due to a higher probability of collusion between metal ions and biosorbents (Onyancha et al. 2008; Dönmez et al. 1999).

Indhumathi et al. (2014) used *Chlorella vulgaris* as adsorbent for chromium removal and achieved 99.75% chromium removal after 60 min at a pH of 3. Chromium can inhibit *Chlorella vulgaris* growth in a dose-dependent manner (Qian et al. 2013). Pagnanelli et al. (2013) found that reducing the ionic strength and increasing the initial chromium concentration resulted in an increase of total Cr removal using algae. Bishnoi et al. (2007) also found that there is a highest initial Cr(III) concentration limit which allowed for the best Cr(III) removal and any further increases in the initial Cr(III) concentration resulted in a decrease percentage removal. The available binding sites on the surface of the algae cell are saturated at a certain Cr(III) concentration, thereby inhibiting further adsorption of Cr(III) ions (Bishnoi et al. 2007). The available sites on the biosorbents are the limiting factor for the biosorption (Akhtar et al. 2008).

Birungi and Chirwa (2014, 2015a, b) tested the ability of three algal species for removal of Cd, La and Tl at an initial concentration of 50 mg/L at a constant biomass and pH. *Stichococcus bacillaris* showed the highest metal removal for Cd at 62.9%, whereas *Chloroidium saccharophilum* had the highest removal of La at 57.62%. All the three species were able to remove 100% Tl (Table 12.3).

12.4.2.3 Immobilisation of Microalgal Cells

Microalgae have a relatively high sorption for removal of heavy metals from wastewater but the main challenge encountered is the free algal cells. Due to the particle size, the free cells have low mechanical strength which makes it difficult to separate the biomass from solution for recycling purposes. The immobilised cells improve operational performance as they provide stability of free cells, hence improving mechanical strength, and can be reused without loss of cells as compared to free cells (Bikram et al. 2014; de-Bashan and Bashan 2010). Various immobilising techniques have been used, for example, crosslinking of cells, encapsulation in polymer gels and entrapment in polymeric matrix. Examples of natural immobilising agents used include alginate, carrageenan, agarose, acrylamide, polyurethane and polyvinyl (Rangsayatorna et al. 2004; Akhtar et al. 2008).

Some of the issues with synthetic immobilisation techniques are the cost of immobilisation agent, disposal after reuse and restricted diffusion due to closed embedding structure. Natural immobilising agents that are eco-friendly and low cost have been suggested, for example, loofa sponge. Some studies have reported

Table 12.3 Adsorption potential for three algal species at initial concentration of 50 mg/L at constant pH and biomass

		Final conc. (mg/L)			Metal removal (%)		
Species	Initial conc. (mg/L)	Cd	La	Tl	Cd	La	Tl
Desmodesmus multivariabilis	50	32.85	33.48	0	34.3	33.04	100
Chloroidium saccharophilum	50	33.2	21.19	0	33.6	57.62	100
Stichococcus bacillaris	50	18.55	22.33	0	62.9	55.34	100

the use of immobilised algal cells using loofa sponge (Table 12.4). It can be noted an increase in the metal uptake with immobilised algae as compared to free cells in all the studies (Table 12.4).

12.5 Bioflocculation

Bioflocculation is an environmentally friendly technology induced by various types of microorganisms (self-flocculating algae, bacteria, fungi or yeast), by extracellular polymer substances or by bioflocculants produced by algae or bacteria (also known as flocculating agents). Compared with the traditional flocculation method, such as metal coagulants, magnetic coagulants, electrocoagulation and ultrasound, bioflocculation is a low-cost harvesting method with no need of additional toxic chemical agents (Zhou et al. 2015; Alam et al. 2016). Recently, several novel approaches based on algal-bacterial, algal-fungal and algal-algal interactions for microalgae harvesting using bioflocculation have been explored (Alam et al. 2016).

12.5.1 Algal-Bacterial Bioflocculation

The mechanisms underlying microalgal bioflocculation via bacterial bioflocculants are poorly understood. Two possible mechanisms are proposed by Wang et al. (2012) and Wan et al. (2013); the first is aggregation triggered by compounds, such as polysaccharides, proteins or other bioflocculant agents produced by bacteria, and the second is aggregation triggered by direct interaction between

Table 12.4 Comparison of free and immobilised algae for metal uptake using loofa sponge

Species	Immobilising agent	Metals	Initial conc. (mg/L)	$q_{\max}$ (mg/g) Free cells	$q_{\max}$ (mg/g) Immobilised cells	References
Chlamydomonas reinhardtii	Loofa sponge	Cd	15–150	23.31	86.21	Birungi and Chirwa (2016)
Chlamydomonas reinhardtii	Loofa sponge	Tl	15–500	1000	5000	Birungi and Chirwa (2016)
Chlorella sorokiniana	Loofa sponge	Ni	2.5–200	45.87	59.58	Akhtar et al. (2004)
Chlorella sorokiniana	Loofa sponge	Cr	100–300	4.97	69.26	Akhtar et al. (2008)
Synechococcus sp. (blue green algae)	Loofa sponge	Cd	10	47.73	57.76	Saeed and Iqbal (2006)

the bacteria and microalgae, which could be facilitated by proteins on the bacterial cell wall or the flagellum.

Wan et al. (2013) found that the bioflocculant could be recovered after filtration and evaporation of the filtrate. The loss of flocculation efficiency in recycling results in only 3%, thereby drastically reducing the cost of the harvesting process. Moreover, the bioflocculant is not toxic to microalgal cells and thus maintains their integrity. However, the large-scale application of microalgal bioflocculation via bacterial is restricted by the need of supplementary substrates and extra energy sources to support bacterial growth, as well as the potential danger of unwanted bacterial contamination of the microalgal production plant (Alam et al. 2016).

12.5.2 Algal-Fungal Bioflocculation

In recent years, several filamentous fungi (*Mucor circinelloides*, *Penicillium expansum* and *Rhizopus oryzae*) were found to be able to form pellets via co-culturing with the non-filamentous microalgae cells under controlled operating conditions (Alam et al. 2016). Zhou et al. (2012) reported that almost 100% of *C. vulgaris UMN235* cells were captured by *Aspergillus* sp. spores onto the pellets within shorter retention time. The fungi-algae pellets can be easily harvested by simple filtration due to their large size (2–5 mm) and their use in the efficient removal of nitrogen and phosphate in wastewater treatment.

Numerous theories have been proposed to explain the algae-fungi pellet formation process; however, the details are still unclear. The mutual attraction through differences in surface charge between microalgae and filamentous fungi cells may be attributed to the co-pellet formation. Several fungi have positively charged hyphae that interact with the negatively charged microalgal cell surface and thus cause flocculation. Moreover, fungal hyphae and mycelia containing polysaccharides with charged active sites may enable surface bio-adsorption. Fungi-assisted algae harvesting technology is an attractive approach in terms of commercialisation, as significantly reducing the production cost. However, the challenge of efficient separation of the fungi and microalgal cells makes this method unsuitable for food or pharmaceutical industries (Alam et al. 2016).

12.5.3 Algal-Algal Bioflocculation

Recently, several self-flocculating microalgae, such as *E. texensis SAG79.80*, *T. obliquus AS-6-1* and *C. vulgaris JSC-7*, have demonstrated their bioflocculating properties (Alam et al. 2016; Zhang et al. 2016), with the ability to aggregate together and form flocs, which facilitate their gravity sedimentation for separation from aqueous solutions. The underlying mechanism, however, is poorly understood and deserves further research (Vandamme et al. 2013). Bridging and patching mechanisms are suggested by several studies on this chemical-free method for flocculating microalgae. When a large network of microalgal cells is formed, the mechanism involved is bridging. If, on the other hand, the cells are more closely attached, the mechanism involved may be patching through the infochemicals excreted by flocculating microalgae (Alam et al. 2016).

There are indications that the infochemicals such as polysaccharides, polyunsaturated aldehydes, glycoproteins and some soluble cell wall proteins isolated from the flocculating microalgae are capable of inducing flocculation in a culture of another species of microalgae (Salim et al. 2011; Taylor et al. 2012; Alam et al. 2014). The bioflocculation of freely suspended microalgae triggered by using the self-flocculating microalgae or infochemicals excreted from flocculating microalgae is particularly interesting and promising. However, the addition of excessive volumes of self-flocculating microalgae for a desirable harvesting efficiency and the additional cost of the production and purification of the infochemicals present a challenge for the industrial application of self-flocculating microalgae (Alam et al. 2016).

12.6 Bio-recovery of Precious Metals and Rare Earths

The efficiency of biosorption exploitation depends on the level of regeneration of biosorbents for reuse in a number of cycles (Bishnoi and Garima 2005). The entire biosorption process consists of adsorption-desorption cycle using various eluents. Selection of a suitable eluent is a challenge and also required for a successful desorption process, which strongly depends on the type of biosorbent and the mechanism of biosorption. The eluents must meet the following requirements: non-damaging to the biomass, less costly, environmental friendly and effective (Vijayaraghavan and Yun 2008; Lesmana et al. 2009). Various chemical reagents have been utilised in the recovery of metals especially dilute acids, e.g. nitric acid (HNO_3), sulphuric acid (H_2SO_4) and hydrochloric acid (HCl). The efficiency of the eluent can be expressed as a solid/liquid ratio (S/L) with the solid representing the metal-laden biomass and the liquid as the eluent. High values of S/L are preferred (Volesky 1987; Kuyucak and Volesky 1989).

12.6.1 Gold Recovery

Recently, freshwater green algae have been demonstrated as efficient adsorbents for gold recovery, with the advantages of their low-cost relative abundance and high binding capacity (Shen and Chirwa 2018a). Other authors also previously reported that the gold (III) were reduced to elemental gold using the dead unicellular algae *Chlorella vulgaris* (Hosea et al. 1986; Greene et al. 1986 and Ting et al. 1995). Their studies suggested that the microalgae rapidly reduced gold(III) to gold(I) and that the algal bound gold slowly reduced to gold(0). Initially, most research focussed on the use of brown and red algae as biosorbent for gold recovery. The bioreduction of gold(III) to gold(0) using the dead biomass of brown alga *Fucus vesiculosus* was investigated by Mata et al. (2009). The recovery and reduction process took place in two stages with an induction period (first stage) lasted about 60 min previous to gold reduction (second stage). The second stage lasted almost 8 h and was characterised by a color change of solution from bright yellow to reddish purple which is associated to gold reduction and the presence of gold nanoparticles.

The similar colour change was observed in the cases of biosorbents using brown alga *Turbinaria conoides* (Vijayaraghavan et al. 2011) and red alga *Chondrus crispus* (Castro et al. 2013). Vijayaraghavan et al. (2011) also found that the biosorption process was rapid and completed within 60 min of contact. After 60 min, *T. conoides* reduced Au(III) to gold nanoparticles. Electrostatic interaction between anion $AuCl_4^-$ and positively charged functional groups, such as amino groups (NH_2) on the algal surface, was proposed to be responsible to the biosorption mechanism. Hydroxyl groups present in the brown algal polysaccharides were involved in the bioreduction of Au(III) to Au(0), which is well in accordance with the previous studies by Mata et al. (2009).

Research effort was more focussed towards recovery of gold nanoparticles deposited on the surface of sorbents but the challenge is how to separate those gold nanoparticles from the metal-laden biosorbents. One method is using the aqua regia to digest the biosorbents to get the gold ions, but its disadvantage is the biosorbents can only be used once. Therefore, recovery of gold via adsorption and desorption before Au(III) reduced to Au(0) offers an alternative option. Ju et al. (2016) reported that over 90% of gold and palladium could be selectively recovered from aqua regia-based metal wastewater by red alga *Galdieria sulphuraria*. These metals were eluted from the algal cells into ammonium solutions containing 0.2 M ammonium salts without other contaminating metals. Shen and Chirwa (2018a) suggested that the freshwater microalga *Tetradesmus obliquus* AS-6-1 is a promising and efficient biosorbent for gold recovery. The level of Au (III) uptake by *T. obliquus* AS-6-1 could approach 15% of the organism's dry weight at the optimum operating conditions. The gold-loaded biomass of *T. obliquus* AS-6-1 was able to be regenerated by 0.1 M thiourea at pH 2.0 and retained good adsorption/desorption capability.

Microprecipitation/bioreduction leading to colloidal or nanoparticle metals on the sorbent is preferable for the recovery of gold in the biosorption process, which has been proposed by many researchers using algae (Greene et al. 1986; Mata et al. 2009; Vijayaraghavan et al. 2011), plants (Gamez et al. 2000) and industrial wastes (Maruyama et al. 2014). The gold(III) ion taken up by those biosorbents was initially reduced to gold(I) and then slowly reduced to gold(0) deposited on the surface of biosorbents with the form of nanoparticles or nanoplates (Greene et al. 1986).

The main functional groups responsible for the reduction of Au(III) to Au(0) on the cell surface are carboxyl and hydroxyl groups which are abundant in polysaccharides of the algal cell wall (Mack et al. 2007; Mata et al. 2009). Furthermore, the electrostatic interaction and ion exchange may also be responsible for the gold binding which was assumed by Ramesh et al. (2008) using chitosan resin and Shen and

Chirwa (2018b) using microalgal adsorbent. It is possible that the combinations of several of these mechanisms are responsible for the gold biosorption, depending on the biosorbents and solution environment. Several studies have been conducted to identify appropriate eluents for the gold recovery as shown in Table 12.5. Because thiourea in acidic solution can form a relatively stable complex with gold(III) and gold(I) and elutes ions efficiently, solution containing thiourea is commonly chosen as eluent for gold desorption (Ju et al. 2016).

12.6.2 Chromium Recovery

NaOH has been found to be effective in recovering Cr(III) but total recovery of Cr(III) is not possible if the absorption mechanism involves surface complexation. A strong alkali desorbent such as NaOH can damage the cell walls of the microalgae (Han et al. 2006). OH− has a strong affinity for Cr(III) and forms $Cr(OH)_4$− readily. Cr(III) cannot be easily replaced by protons; thus HCl is not very effective desorbent. However, some studies have found that nitric acid, HNO_3, was also an effective desorbing agent and that the microalgae retained their biosorption capacity after desorption, but at high HNO_3 concentration (>0.1 M) serious damage was done to the microalgae and subsequently lost its biosorption capacity (Akhtar et al. 2008; Chojnacka et al. 2005). Shokri et al. (2015) also found that the green microalgae were regenerated when using HNO_3 as a desorbent for Cr(III) desorption. Cr(VI) is considered a strong oxidation agent; therefore a biosorbent that is more oxidation resistant will be easier to recover. If algal bound Cr(VI) is reduced to Cr(III), then the recovery of Cr(VI) ions is limited but the recovery of Cr(III) is possible (Cabatingan et al. 2001).

12.7 Conclusion

Green technology using phycoremediation and phytoremediation is a current technology that has been recognised for a long time as an alternative for treatment of wastewater containing heavy metals. Various macro- and microorganisms have been tested especially at laboratory scale to determine the sorption potential of heavy metals and recovery of precious and rare metals. The hyperaccumulators which are extremely resistant to high metal concentration can be used for ecosystem restoration over a long period of time. Various technologies including bioaccumulation, biosorption and bioflocculation show potential for commercial application to industry. Microalgae are widely studied due to their notable adsorption of heavy metals and recovery of target elements compared to other microorganisms. The main challenge that could affect the utilisation of microalgae at industrial scale is determining less costly and eco-friendly immobilising agents to improve the mechanical strength for reusability purposes. There is, therefore, a need to undertake more pilot studies

Table 12.5 Eluents for different gold-loaded adsorbents

Biosorbent	Eluent	Desorption performance	References
Chlorella vulgaris	Thiourea, mercaptoethanol	Algal-bound Au and Hg can be selectively eluted by mercaptoethanol	Darnall et al. (1986)
Sargassum natans	Thiourea	Maximum desorption was achieved with 0.1 M thiourea containing 0.02 M $NH_4Fe(SO_4)_2$	Kuyucak and Volesky (1989)
Immobilised persimmon tannin	1 M thiourea	Almost 100% of gold desorption in the five adsorption/desorption cycles	Nakajima and Sakaguchi (1993)
Eggshell membrane	NaOH, NaCN	>95% of gold(I) desorption using 0.1 M NaOH; >92% of gold(III) desorption using 0.1 M NaCN	Ishikawa et al. (2002)
Chitosan resin	0.5 M thiourea + 0.2 M H_2SO_4	Adsorption/desorption cycles up to four runs	Donia et al. (2007)
Activated carbon derived from hard shell of apricot	Acetonitrile, acetone, methanol, ethanol, isopropanol	Near 90% of gold desorption using 40% acetone. The capacity of gold desorption using these eluents was in the order: Acetone > acetonitrile > methanol > ethanol > isopropanol	Soleimani and Kaghazchi (2008)
Sargassum biomass	NaOH	Maximum desorption of 97.8% was achieved with 2 M NaOH	Sathishkumar et al. (2010)
$Fe_3O_4@SiO_2$ nanoparticles	Thiourea + HCl	96.2% of gold desorption using 2% of thiourea containing 1 M HCl	Zhang et al. (2013)
L-cysteine impregnated alginate capsules	Thiourea + HCl	98.5% of gold desorption was achieved by 0.1 M thiourea in 0.1 M HCl	Kotte and Yun (2014)
Red alga, *Galdieria sulphuraria*	HCl, $NH_4Br + NH_3$, $NH_4Cl + NH_3$, KOH, thiourea + HCl	78% of Au^{3+} was eluted by 1 M thiourea and 0.1 M HCl with the elution of other contaminating metals; 48% of Au^{3+} was eluted by 0.2 M NH_4Cl with 2.8% NH_3 without the elution of other contaminating metals	Ju et al. (2016)
Freshwater Microalgae *Scenedesmus obliquus AS-6-1*	Thiourea at different pH	Desorption efficiency retained 95%, 94% and 88% in three adsorption/desorption cycles, respectively, using 0.1 M thiourea at pH 2.0	Shen and Chirwa (2018a)

as most studies were undertaken in the laboratory to establish the cost implications of using bioremediation technologies compared to traditional technologies without compromising the environment. In addition, there is a need to determine the longevity of reuse of the biosorbents as disposal becomes a secondary problem.

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Chapter 13
Green Synthesized Nanoparticle-Mediated Wastewater Treatment

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Abstract Freshwater in the environment is getting contaminated day by day due to constant pollution of freshwater bodies through different anthropogenic sources which leads to scarcity of freshwater for the people usage. Green synthesis of nanoparticle is a very efficient method of nanoparticle synthesis. Nowadays these nanoparticles are used to treat wastewater system. The overview of recent advancement in nanotechnology for water and wastewater treatment mechanisms is provided, including nanobased materials, such as nanoadsorbents, nanometals, nanomembranes, and photocatalysts. Various advantageous roles governed of these materials as well as technical barriers when compared with conservative processes are being demonstrated. The commercial value of these materials is presented and viewpoint on further research value is given for each type of nanobased material and process. This chapter includes recent trends in green synthesis of nanoparticles using different plants and their parts like leaves, stem, etc., and their application in treatment of wastewater.

Keywords Wastewaters · Industries · Nanoparticles · Green synthesized · Treatment

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13.1 Introduction

The freshwater is essentially significant for humans, animals, and plants, not just for drinking, but also for irrigation, domestic use, and other vital activities. It is expected to become increasingly inadequate in the near future, and this is partly because of environmental change (Pretty 2007). Due to the rapid increase in world population as well as global warming, water reservoirs are decreasing at a very fast rate. In this approach, discreet use of water resources and reuse of treated wastewater for various purposes have been perceived as the best method for monitoring the restricted resource of freshwater (Shittu and Ihebunna 2017). The occurrence of microorganisms and trace metals is the principle indication of water contamination. The trace metal contamination of water is a public health concern, with several health risks associated with it (Bharagava et al. 2018; Kishor et al. 2019; Rahman and Singh 2018). The prokaryotic organisms, for example, *Escherichia coli*, *Shigella* spp., *Salmonella* spp., *Vibrio* spp., and *Cryptosporidium*, are known to be transmitted by water and cause ill-health when this water defiled by microorganisms is consumed (Ashbolt 2004).

Nowadays, metal nanoparticles especially gold and silver NPs are of particular interest to researchers due to their specific properties and wide applications in the field of medical sciences. Biosynthesis approach of NPs is considered as a better alternative than physical and chemical method (Ahmad et al. 2003; Song et al. 2010; Gautam et al. 2018) as it is eco-friendly, cost effective, and less time requiring. Different materials are categorized as biological for nanoparticle synthesis; these include plant extracts, microscopic organisms, growth chemicals, and actinomycetes (Bharagava and Chandra 2010; Chandra et al. 2012; Agarwal et al. 2017). But plant extracts have been the major focus due to their abundant nature and the phytochemical composition (Bharagava et al. 2008).

There is constrained chance of an expansion in the supply of freshwater due to ever-increasing demand by growing population throughout the world; additionally, water-related issues are anticipated to increase further because of atmospheric changes and because of population growth throughout the following two decades (Vörösmarty et al. 2000). It is evaluated that overall population will increment by about 2.9 billion as of now till 2050 (as indicated by UN's normal projections) (Rockström 2003). Nanotechnology has been considered as a useful method for identifying and solving problems related to the water quality (Bottero et al. 2006). Nanomaterials are adding to the improvement of progressively effective treatment forms among the new water system (Obare and Meyer 2004).

There are numerous parts of nanotechnology that address the different issues of water quality so as to make sure the ecological stability is maintained. This information gives a unique point of view on fundamental research of nanotechnology for water/wastewater treatment and reuse by concentrating on difficulties of future research. Advancement in the field of nanoscience technology and designing propose that huge numbers of the flow issues including water quality could be resolved or greatly diminished by utilizing nanoadsorbents, nanocatalysts, bioactive nanoparticles, nanostructured synergist layers, nanotubes, attractive nanoparticles, granules, chip, high surface region metal molecule supra subatomic assemblies with trademark length sizes of 9–10 nm including clusters, small-scale particles, nanoparticles, and colloids which significantly affect water quality in natural environment (Diallo and Savage 2005).

13.2 Green Synthesis of Nanoparticles

Nanoparticles can be prepared by various methods which are usually categorized in to two major synthetic routes which are the top-down and the bottom-up approaches (Fig. 13.1) (Rahman and Padavettan 2012). In the top-down (physical) approach, nanoparticles are obtained from their bulk materials (macroscopic) using different methods and techniques like mask, ball milling thermal decomposition, irradiation, laser ablation, arc discharge, etc. (Mijatovic et al. 2005). In bottom-up (chemical and biological) approach, nanoparticles are obtained from their atomic level building blocks which react to generate nanoparticles of the desired shape and size. These methodologies utilize larger of nanostructures (Barth et al. 2010). During self-gathering the physical forces working at the nanoscale are utilized to join fundamental units into bigger stable structures. Physical and chemical methods are being utilized broadly for generation of metal and metal oxide nanoparticles as shown in Fig. 13.1 (Ma et al. 2017). However, these methods of production require the use of highly reactive and toxic reducing agents such as sodium borohydride and hydrazine hydrate, which account for undesired detrimental impacts on the environ-

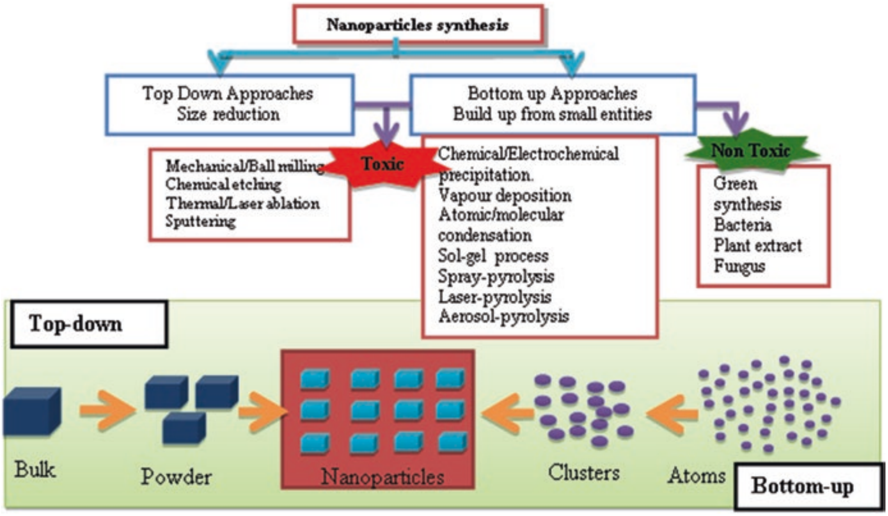

Fig. 13.1 Top-down and bottom up approaches of nanoparticles synthesis involving their toxic and nontoxic effects

ment, plant, and animal life (Saif et al. 2016). Researchers are putting continue efforts to develop facile, effective, and reliable green chemistry processes for the production of nanomaterials.

Different organisms behave as clean, eco-friendly, and sustainable precursors in order to produce stable and well-functionalized nanoparticles. These may incorporate bacteria, actinomycetes, fungi, yeast, viruses, etc. Therefore, it is critically important to develop a more reliable and sustainable process for the synthesis of nanomaterials. The idea of economic viability, ecological sustainability, and social adaptability as well as the availability of local resources should be kept in mind during the production of nanomaterials (Saif et al. 2016). In order to keep the cost of the final completed nanotechnology-based products affordable to consumers, industries must maintain a delicate balance between environmentally sound green processes and their sustainability. The green nanotechnology-based production processes operate under such conditions where the involvement of toxic chemicals is negligible. Metal NPs have been extensively studied because of their specific characteristics such as catalytical, optical, electronic, antimicrobial, and magnetic properties.

Among noble metals, silver is the metal of preference in the field of biological systems, living organisms, and medicine (Bootharaju et al. 2017). The biosynthesis of nanoparticles involves use of biogenic matter including plant extracts, biopolymers, and microbial residue like bacteria, fungi, algae, and yeast for nanomaterial fabrication (Sharma et al. 2015). Development of biocompatible, nontoxic, and eco-friendly methods for the synthesis of nanoparticles is mainly concerned in green chemistry (Narayanan and Sakthivel 2010). Biosynthesis of metal nanoparticles using plants is currently under exploitation. The biological synthesis of metal nanoparticles (especially gold and silver nanoparticles) using plants (inactivated plant tissue, plant extracts, and living plant) has gained more attention as a suitable alternative to chemical procedures and physical methods (Iravani 2011). Synthesis of metal nanoparticles using plant extracts is quite cost effective and therefore can be used as an economic and useful alternative for the large-scale production of metal nanoparticles. Extracts from plants may act as both reducing and capping agents in nanoparticle synthesis. The bioreduction of metal nanoparticles by combinations of biomolecules found in plant extracts (e.g., enzymes, proteins, amino acids, vitamins, polysaccharides, and organic acids such as citrates) is environmentally beneficial, yet chemically complex (Sharma et al. 2009).

Because of the important and critical role of plants in biosynthesis of metal nanoparticle production, the green synthesis of metal nanoparticles using plants has been discussed in this part. Current research in biosynthesis of nanometals using plant extracts has provided a new opportunity in fast and nontoxic methods for production of nanoparticles. Many researchers have reported the biosynthesis of metal nanoparticles by plant leaf extracts and their subsequent potential applications (Ghosh et al. 2012). MubarakAli et al. (2011) have studied the bioreduction of gold and silver ions by leaf broth of *Pelargonium graveolens* and *Azadirachta indica* (Thakkar et al. 2010). Moreover, they have explored the formation mechanism of triangular gold nanoprisms by *Cymbopogon flexuosus* (lemongrass) extracts where the nanotriangles seemed to grow by a process involving rapid bioreduction, assembly, and room temperature sintering of “liquid-like” spherical gold nanoparticles (Brumbaugh et al. 2014).

Also rapid synthesis of stable gold nanotriangles can be achieved which involves the use of *Tamarindus indica* (tamarind) leaf extract as a reducing agent (Kumar and Yadav 2009). The shape of metal nanoparticles subsequently changed their optical and electronic properties (Storhoff et al. 2000). They have also demonstrated the synthesis of gold and silver nanoparticles having variety of shapes (spherical and triangular) and sizes using *Aloe vera* plant extracts (Bar et al. 2009). It was explained that only biomolecules having molecular weight less than 3 kDa caused reduction of chloroaurate ions, leading to the formation of gold nanotriangles. Nevertheless, the bioreduction of silver ions proceeded barely in the presence of ammonia. The aqueous solution of gold ions when exposed to *Coriandrum sativum* leaf extract was reduced and resulted in the extracellular biosynthesis of gold nanoparticles with spherical, triangle, truncated triangle and decahedral morphologies ranging from 6.75 to 57.91 nm. These nanoparticles were stable in solution over a period of 1 month at room temperature (Korbekandi et al. 2009).

Njagi et al. (2010) used aqueous *Sorghum* sp. (hybrid sorghum) bran extract for nZVI synthesis; eucalyptus globulus leaf extract was used as a bioreducing agent to synthesize nZVI. P. Wang synthesized iron nanoparticles using *Eucalyptus* leaf extract by adding 0.1 M $FeCl_3$ solution in a ratio of 1:2; Wang et al. synthesized polydispersed iron nanoparticles employing *Eucalyptus* leaf extract obtained from its leaf litter. nZVI, Fe_3O_4, and Fe_2O_3 were the different forms of nanoparticles synthesized during the process; FeO/Fe_3O_4 nanoparticles were successfully synthesized using pomegranate leaf extract by Rao et al. (2013); these nanoparticles were coated on two strains (NCIM 3589 and NCIM 3590) of heat-killed yeast cells *Yarrowia lipolytica*, which is considered a good biosorbent itself; Venkateswarlu et al. (2014) used plantain peel extract as a low-cost bioreducing agent for synthesizing magnetite nanoparticles.

Iron salt solution was hydrolyzed which led to the formation of ferric hydroxide, and then it was subsequently reduced by various biomolecules to form Fe_3O_4 nanoparticles, banana peel ash extract was used to synthesize iron oxide nanoparticles, and aqueous extract of *Colocasia esculenta* leaves was used to reduce graphene oxide by Thakur and Karak (2014). Daniel et al. (2013) used leaf extract of the evergreen shrub *Dodonaea viscosa* to synthesize iron nanoparticles where the effect of leaf extract concentration on nanoparticle synthesis was studied. Senthil and Ramesh (2012) reported the green synthesis of Fe_3O_4 nanoparticles at room temperature using leaf extract of *Tridax procumbens*, and Narayanan et al. (2011) synthesized superparamagnetic magnetite/gold (Fe_3O_4/Au) hybrid nanoparticles at room temperature using grape seed proanthocyanidin (GSP) for the first time. Machado et al. (2014) screened leaf extracts of 26 plants for the production of nZVI. During synthesis variables like leaf extraction, temperature, time, and leaf mass to solvent volume ratio were checked. Eighty degree Celsius was identified as the optimum temperature, whereas the other variables like extraction, time, and leaf mass to solvent volume ratio varied as per leaf type.

In another study, Machado et al. (2014) synthesized nZVI using grape marc, black tea, and vine leaf extract. Kumar et al. (2013) synthesized stable iron oxide (Wustite) using aqueous extract of *Terminalia chebula* dry fruit pericarp. Leaves of three plants native to Australia, namely, *Eucalyptus tereticornis* (A), *Melaleuca nesophila* (B), and *Rosmarinus officinalis* (C), were explored by Wang et al. (2014). Phumying et al. (2013) synthesized Fe_3O_4 nanoparticles by the hydrothermal method using *Aloe vera* plant extract. Ahmmad et al. (2013) successfully synthesized highly pure hematite (α-Fe_2O_3) nanoparticles by the hydrothermal method using green tea (*Camellia sinensis*) leaf extract. Nanoparticle synthesis was carried out by exposing pretreated and milled powder of *Medicago sativa* (Alfalfa) to the salt solution of ferrous ammonium sulfate.

13.3 Use of Various Green Synthesized Nanoparticles in Wastewater Treatments

Treating polluted water has become a major challenge as various heavy metals and pathogenic organisms cause human health problems and can present a major threat to the environment (Ayangbenro and Babalola 2017). The use of magnetite nanoparticles as a sorbent has shown promise as an emerging treatment of polluted water. In this study, a common weed plant (*Lantana camara*) was used for synthesis of magnetite nanoparticles (MNPs). Synthesized MNPs were characterized for physical properties and batch absorption studies were undertaken to assess the potential for removal of heavy metals, namely, lead, under varying conditions (Sun et al. 2011). Nanotechnology can enable a distributed water reuse and treatment paradigm and offer leapfrogging opportunities to obviate concerns of water quality degradation within distribution networks, alleviate dependence on major system infrastructure, exploit alternative water sources (e.g., recycled new water) for potable and agricultural use, and abate energy consumption.

This vision may be particularly appropriate for developing countries that face rapid degradation of water quality with increasing pressure for cleaner water to meet more stringent environmental, public health, and food safety standards. This scenario underscores the need for a new class of “high-performance” water treatment technology. Future urban systems in developing countries will likely increasingly rely on nanotechnology-enabled water monitoring, treatment, and reuse systems that target a wide variety of water pollutants and are affordable and easy to operate. This will also contribute toward a zero discharge paradigm, which is an ultimate goal of sustainable urban water management. Examples of engineered nanomaterials (ENMs) that can enable this vision are summarized in this chapter. Such novel technologies for water treatment at both point of use and community scale are of great value for increasing the effectiveness and robustness of water distribution networks, allowing access to clean water to users that are not connected to a central network, and for emergency response following catastrophic events.

Various industries such as paper and pulp, textile, tanneries, cosmetic, coffee pulping, pharmaceutical food processing, electroplating, and dye manufacturing units discharge colored and toxic effluents to water (Erdem et al. 2005; Hameed 2009; Chandra et al. 2011; Zainith et al. 2019; Kishor et al. 2019). The untreated wastewater containing colored compounds which have complex structures is difficult to biodegrade. Some dyes used in the textile industries are toxic and carcinogenic, which present eco-toxic hazard and introduce the potential danger of bioaccumulation and also affect humans through the food chain (Babu et al. 2007; Sujata and Bharagava 2016; Kishor et al. 2019). Green synthesized NPs are highly proficient for recycling and removal of heavy metal from wastewaters without loss of their stability and degradation of a variety of organic pollutants from wastewaters and, thus, purify the wastewaters for reuse and recycling and could solve various water quality issues worldwide.

Nickel oxide is considered as good adsorbent due to its chemical and magnetic properties (Nateghi et al. 2012). Rafique et al. (2012) synthesized nano NiO using coprecipitation method and the obtained particles were probed for their adsorption nature toward sulphate and nitrate. It was noted that the adsorbent was effective at pH 7 for the removal of both anions from waters. The synthesized silver nanoparticle also shows heavy metal removal activity in laboratory simulated wastewater. The safety toxicity studies show no significant difference between the orally administered silver nanoparticle-treated water group and control group, while the histopathological studies show well-preserved hepatic architecture for the orally administered silver nanoparticle-treated wastewater group when compared with the control group.

Therefore, it can be concluded that the biosynthesized silver nanoparticles have efficient ability in heavy metal removal without subchronic adverse effects in experimental rats (Shittu and Ihebunna 2017). As water becomes scarcer and more contaminated, the food industry stands to gain much from advanced technology that would provide cleaner and more plentiful water supplies. Nanotechnology has the potential to meet these water-related needs in an inexpensive, efficient, yet flexible way that is crucial for developing nations. Wang et al. (2014) utilized the leaf extracts of green tea and eucalyptus separately for the formation of iron nanoparticles (Fe NPs) and employed for the efficient removal of nitrate from wastewater. Synthesis of spheroidal iron nanoparticles (Fe NPs) was confirmed by employing characterization techniques. A comparison study was conducted between plant-synthesized and chemically synthesized iron materials. Green tea and eucalyptus-mediated Fe NPs were able to remove 59.7% and 41.4% of nitrate from wastewater, respectively, compared to 87.6% and 11.7% removal of nitrate by nZVI and Fe_3O_4 nanoparticles, respectively.

Despite the higher removal efficiency of nZVI, the green synthesized Fe NPs were found to be more stable in nature. Reactivity of aged nZVI, green tea, and eucalyptus synthesized Fe NPs was compared after being completely exposed to air for 2 months. Green tea and eucalyptus synthesized Fe NPs retained the same efficiency of 51.7% and 40.7%, respectively, whereas the efficacy of nZVI significantly dropped about 2.1-fold (45.4%). New study, a green one-pot synthesis of L-serine

(L-Ser) capped magnetite nanoparticles (Fe_3O_4 NPs) and its potential application for adsorption of RhB dye from aqueous solution (Belachew et al. 2017).

13.4 Conclusion and Future Prospective

This chapter highlights the recent advancement in deciphering iron NP synthesis by plant extracts and their applications in water and wastewater treatment. Use of physical and chemical methods for NP synthesis is common but recently several new eco-friendly and economically feasible synthesis techniques are being explored. Green synthesized NPs are being effectively exploited in the area of medical and environmental remediation. Green synthesized NPs and several characterization techniques are currently being utilized in water and wastewater treatment because of their high proficiency and biocompatible nature. Green synthesized NPs are greatly proficient in recycling and eradication of heavy metal contaminants from wastewaters without disrupting their stability, consequently, for purification of wastewaters for reuse and recycling could solve numerous water quality problems globally. Moreover, experiments and problems correlated with the use of green synthesized Fe NPs in water and wastewater treatment are also discussed. However, the enormity of future research scope in this field cannot be accentuated enough.

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Chapter 14
Microbial Communities in Constructed Wetland Microcosms and Their Role in Treatment of Domestic Wastewater

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Abstract Microbial biomass is the main reducer for majority of organics and nutrients. The aerobic region of constructed wetland microcosms (CWMs) is majorly characterized by presence of *Nitrosomonas* and *Pseudomonas spp.* The diversity of ammonia-oxidizers mainly *Nitrosospira sp.* is higher in CWMs designed to treat domestic wastewater as compared to other bacteria studied. The activity of enzymes within CWMs is a key indicator towards role of microbial community. Rhizospheric region has diverse elements that comprises minerals, sugars, vitamins, organic acids, polysaccharides, phenol and various other organic materials that encourages the microbial groups to degrade wastewater pollutants. The presence of macrophytes has significant effects on microbial richness and community structure. The root exudates liberated by macrophytes are also able to alter the richness and diversity of the microbial population. The decomposition rates of microbes become slow as temperatures drop, which can be optimized by increasing the size of wetlands to accomplish the slower reaction rates. The pH of wastewater has also a strong effect on various microbially mediated reactions and processes. Temperature, hydrologic conditions, macrophytic diversity/richness and biotic succession strongly impact the microbial community structure. A little alteration in the diversity or community structure of the microorganisms directly affects the treatment performance of CWMs.

Keywords Microbial diversity/richness · Constructed wetland microcosms · Removal efficiency · Enzyme activity · Macrophytes

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14.1 Introduction

Water scarcity is the major driver of wastewater reclamation, particularly in arid and semi-arid zones. Reclamation of wastewater has turned out to be an alternate source of water supply for several non-potable requirements in several countries including the USA (US Environmental Protection Agency (US EPA), National Risk Management Research Laboratory, US Agency for International Development 2012; World Bank Group 2013). In the USA, around 7–8% of wastewater after treatment through Constructed Wetlands (CWs) has been reused mostly for agriculture and urban irrigation (US Environmental Protection Agency (US EPA), National Risk Management Research Laboratory, US Agency for International Development 2012). In North Africa, majority of wastewater reused in agriculture and for landscaping entails many undesirable effects on human and ecosystem health (World Bank Group 2013). In the United Arab Emirates (UAE), majority of the wastewater treatment is followed by biological means and utilized to reform the landscape (AlMulla 2016). Around 70% of wastewater generated from household activities in Israel has been reused for several activities (US Environmental Protection Agency (US EPA), National Risk Management Research Laboratory, US Agency for International Development 2012).

Many water reuse programs were initiated in the USA towards expensive nutrient removal mechanisms from secondary wastewater, consequently removing or decreasing wastewater discharge. Climate change and environmental sustenance concerns play a key role in reclamation of wastewater (Tram Vo et al. 2014). During previous decades, policy developers in several nations have expressed plans/guidelines favoring development and implementation of projects linked with reclamation of wastewater. World Health Organization (WHO) provided guiding principles related to human health by the wastewater used for agricultural and aquacultural activities in 1989 which was amended in 2006 for the proper and safe use of wastewater (WHO 2006). Around 30 states and one territory of US till September 2012 have implemented guidelines and 15 states have designed standards that administrate water reuse. China has reformed its water policy to boost the utilization of treated wastewater (Chang et al. 2013).

The Australian council of engineering and innovation has developed wastewater reuse guidelines for metropolitan wastewater improvements (Radcliffe 2006). The Royal Decree (RD) of Spain has recognized the legal charter for reuse of wastewater (Vera et al. 2013; Avila et al. 2015). Constructed wetland microcosm (CWM) is a shallow basin occupied with substrate material, generally soil, gravel, or sand, and planted with macrophytes that can adopt indigenous climatic settings and stand with waterlogged situations (Kumar and Dutta 2019a). A working model of CWM is shown in Fig. 14.1. The microbial biomass is the main known factor for removal of organics and nutrients. Particulate and dissolved organics are actively converted into CO_2 and water by bacteria, fungi and actinomycetes. Macrophytes play a vital role in removal processes by diffusing atmospheric oxygen (O_2) into their root system that are used by the microbes to decompose wastewater contaminants.

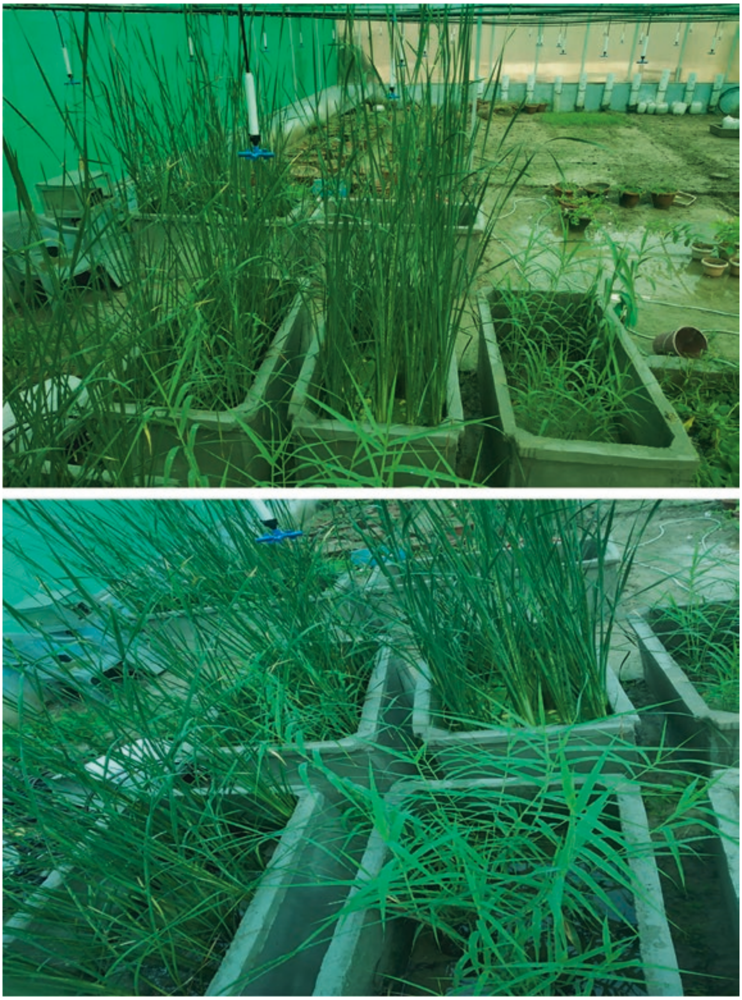

Fig. 14.1 CWM units working successfully for the treatment of domestic wastewater at Babasaheb Bhimrao Ambedkar University, Lucknow

Macrophytes provide several functions such as stabilization of the surface of beds, clogging prevention, offers opportunity for physical filtration, insulation during winters, and provide surface for microbial attachment (Valipour and Ahn 2016).

Basically, the contaminants removal comprises three processes namely biological, physical and chemical methods. Physical processes comprise mainly filtration and sedimentation. Chemical processes include bio-transformation, dividing unionized and ionized acids and bases, cation exchange, solubility of solids and gases. Nitrification, denitrification, photosynthesis, respiration, fermentation, and microbial phosphorus eliminations are biological process (Mitchell and McNevin 2001). The functions of CWMs are extremely dependent on microbial population such as bacteria, fungi and protozoans and their metabolic rate (Wetzel 1993). Pollutants transformation is the major microbial mechanism which directly takes part in treatment of wastewater and alters the redox potential of the substrate (Kumar and Dutta 2019b). In fact, microorganisms self-sustain according to the features of supporting media and remain in dormant stage for several years if ecological conditions are unfavorable (Hilton 1993). It is known that noxious elements like heavy metals and pesticides might have deleterious effects on microbial population present in a CWM. Activity of microbes also gets influenced by the oxygen in the root zone.

Rhizospheric region is well known for their rich microbial activities such as macrophyte–microbe interactions and interaction with supportive materials and pollutants. It is the area where majority of biological reactions take place because of close interaction among supportive materials and roots of macrophytes. It is also recognized as a region with diverse elements such as minerals, vitamins, sugars, organic acids, phenol, polysaccharides, carbon compounds and enzymes and various other materials that encourage the microbial groups to degrade organic pollutants (Bertin et al. 2003; Faulwetter et al. 2009; Miersch et al. 2001). A diverse range of microorganism groups perform and influence the performance of CWMs (Dong and Reddy 2010; Ibekwe et al. 2003; Long et al. 2016). Mobilizing of nutrients is facilitated by the rhizodeposition products. Hoffland et al. (1992) evaluated that the solubility of iron and phosphate was increased by organic acid produced by different plants under nutrient limiting conditions; therefore, the nutrient uptake capacity of macrophytes is improved.

Microbial population used organics as substrates and expelled vitamins to encourage growth of microbes that is known as ‘rhizosphere effect’. Microorganisms attached with the substratum develop biofilms that are habitually present inside a self-produced medium of extracellular polymeric substance (EPS) (Kumar and Dutta 2019b). Most of nitrogen from wastewater is removed by microbial communities by influencing anammox and nitrification-denitrification mechanisms within CWMs (Kröger et al. 2012; Oehl et al. 2004). However, removal of phosphorus through mineralization and immobilization is also partially affected by microbial activities (Truu et al. 2005).

14.2 Microorganisms in CWMs and Their Role in Treatment Process

Characterization of the microbial groups in CWMs offers valuable information about understanding their role in treatment efficiency (Zhong et al. 2015). The microorganisms require 75–100 days to develop communities in CWMs system with sand filters (Truu et al. 2009; Weber and Legge 2011), in which denitrifying bacteria take 75 days and ammonium- oxidizing bacteria require 95 days for their development (Wang et al. 2016). Polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE) is an advantageous tool for evaluating diversity of microbial community and their structure in CWMs (Ibekwe et al. 2003). This technique was firstly applied by Muyzer et al. (1993) in microbial ecology, and later by Adrados et al. (2014) to evaluate the structure of bacterial community in CWs. Additional significant mechanism is microbial biomass carbon (MBC) that is generally used to measure microbial biomass.

MBC is a subsidiary method to measure the microbial density and has been considered to be a valuable parameter for assessing the contaminant removal effectiveness in CWs (Truu et al. 2009). Therefore, the MBC can offer meaningful information about the microbes in CWs. However, several studies on MBC have been directed toward their relevance to environmental factors, such as land use, macrophytic species and seasons (Calheiros et al. 2009a, b). Earlier findings revealed that the microorganisms show diverse characteristics for the elimination of contaminants (Ahn et al. 2007; Krasnits et al. 2009). These microorganisms have been regarded as the main determining factor for water quality enhancement (Calheiros et al. 2009a, b; Faulwetter et al. 2009). Several other factors such as temperature, macrophytic diversity (Zhang et al. 2010, 2011a, b), hydrologic conditions (Mentzer et al. 2006; Steenwerth et al. 2006), and biotic succession (Kent et al. 2007) impact the structure of microbial community. The quantity of oxygen and root exudates useful for microorganisms in the rhizospheric zone has been found to differ by macrophytic species (Laskov et al. 2006). Majority of bacterial population is found in the rhizosphere region.

Several studies reported that the *Nitrosomonas* species is dominant in the plant roots zone, increasing the removal of nitrogen (Puigagut et al. 2008). Appropriate macrophyte species is vital to determine the microbial structure that is eventually responsible for the removal process. It is reported that the macrophytes which are able to tolerate high salinity (halotolerant), advance the treatment efficiency of CWMs (Wiessner et al. 2005; Wu et al. 2009), through liberating oxygen and making healthier environments for aerobic halotolerant microorganisms (Wu et al. 2012; Xiong et al. 2011). The arrangement of microbial groups in different zones of soil substrate in CWMs designed for the treatment of domestic wastewater was observed by Truu et al. (2005). Later they found that the wetland depth is a key component that affects the activity and community structure (Truu et al. 2009). Several previous investigations have reported microbial diversity in laboratory scale as well as in full-scale CWs (Calheiros et al. 2009a, b; Krasnits et al. 2009; Sleytr et al. 2009; Dong and Reddy 2010; Zhang et al. 2010).

However, the information about how the diversity of microorganisms changed in the long-term operations is still inadequate (Adrados et al. 2014). The roots of macrophytes play a central role in developing structure of bacterial community (Faulwetter et al. 2013). Zhang et al. (2011a, b). It is confirmed that root exudates of macrophytes such as *Thalia dealbata* inhibited the growth and development of the Cyanobacteria. Presence of excess nutrients and other noxious substances in a wetland system distresses the biofilms and their arrangements (Calheiros et al. 2009a, b). The study carried out by Llanos-Lizcano et al. (2019) characterized a total of 180 (65 anaerobic and 115 aerobic) heterotrophic bacteria from rhizosphere of *C. articulatus* and *Thalia geniculata* together with non-planted constructed wetland, in which water flows horizontally.

Peralta et al. (2013) also described parallel outcomes about the bacterial communities in different types of constructed and natural wetlands; they also found that the α-Proteobacteria was the most dominant class, followed by γ-Proteobacteria and β-Proteobacteria. CWMs with different phosphorus loading rates were characterized for microbial populations by Ahn et al. (2007) using length heterogeneity PCR (LH-PCR) relay on the 16S rRNA gene. The outcome of this study was that the sediment has abundant α-Proteobacteria (about 48–60%) and then Actinobacteria and Firmicutes and remains constant throughout the study. Several other researchers have evaluated numerous connections between bacterial diversity, pollutants loading rates and removal efficiencies in CWMs (Wu et al. 2016; Zhi et al. 2015; Zhang et al. 2016).

14.3 Microbially Mediated Reactions in CWMs

The filtration is the most significant removal mechanism working in CWMs, whereas some microorganism-mediated procedures, biochemical networks, sedimentation, volatilization, photodegradation, sorption, transpiration flux and plant uptake also enhance the performance (Bitton 2005; Morvannou et al. 2014). It is reported that some bacterial populations in animal waste actively function for decomposition of several organic compounds and to suppress pathogens. One such bacterial group namely chemolithotrophic ammonia-oxidizing bacteria take part in several chemical and biological breakdown of ammonium. They are responsible for conversion of ammonium (NH_4) to nitrate (NO_3) through nitrogen cycling (Behrends et al. 2001; Ansola et al. 2014). Oved et al. (2001) reported the influence of urban wastewater on the function and community structure of these bacteria in soil substrate via denaturing gradient gel electrophoresis (DGGE).

The result showed a substantial and constant change in the structure of communities of these bacteria with *Nitrosomonas* dominated effluent. It is also reported that the diversity of these ammonia-oxidizing bacteria mainly *Nitrosospira sp.* was higher in CWMs as compared to other bacteria studied. Therefore, it is evaluated that the diversity of ammonia-oxidizing bacteria inside a constructed wetland system play key role on its stability (Rowan et al. 2003). Basically, there are six key biological processes employed in the treatment of wastewater; these are microbial phosphorus elimination, nitrification, denitrification, fermentation, respiration and photosynthesis (Mitchell and McNevin 2001). Wastewater that is heavily loaded with biological oxygen demand (BOD) and chemical oxygen demand (COD) is usually undergo oxidation and methanation process supported by oxygen and sulfur loving bacteria (Chan et al. 2008).

Oxygen enters into the deposits of the supportive materials with the assistance of macrophytic roots and produce an aerobic zone nearby roots. This region is characterized by presence of *Pseudomonas aeruginosa spp.* and *Nitrosomonas* that are accountable for the aerobic breakdown of contaminants. The anaerobic zone is characterized by the dominance of methanogens and sulfur degrading bacteria. Degradation of contaminants anaerobically involves mainly two-steps, first one is fermentation and the other one is methanogenesis (Cui et al. 2010; Pedescoll et al. 2011). An ultimate characteristic of CWMs is that their roles are controlled mainly through microbial population and their metabolic rate (Wetzel 1993). Microbial population chiefly includes bacteria, fungi, protozoa, rind algae and yeasts. The biomass of microorganisms is a main reducer for majority of organics and nutrients. The activity of microorganisms converts several organic and inorganic materials into innocuous insoluble materials, and, changes the redox reaction (reduction/oxidation) of the media material.

The transformations are either aerobic or anaerobic. Aerobic settings are commonly described to be more efficient for the removal of maximum organic contaminants. It is reported that the rate of nitrification-denitrification with two macrophytic species are much higher than CWMs with one or without macrophyte (Hua et al. 2017). The macrophytic type, density and their distribution can affect contaminants removal due to alteration in bacterial communities and consecutive aerobic and anaerobic settings (Calheiros et al. 2010; Zhu et al. 2017). It is known that the lower concentrations of nitrogen can also affect the removal efficiency.

14.4 Seasonal Variability Among Microbial Communities with Respect to Macrophytes

The structure of microbial population may vary widely according to the change in environmental conditions. In summer season, *Phragmites australis* contained dominant microbial groups (e.g., actinobacteria, bacteroidetes, and proteobacteria). However, unplanted units possess maximum photosynthetic bacteria and cyanobacteria (Wang et al. 2016). The richness of proteobacteria with *Phragmites australis* during winter season was >40% and intensely declined in unplanted units. Moreover, the abundance of cyanobacteria and photosynthetic bacteria declined in unplanted units. In both periods, bacteria remained more dominant in root zone as compared to supportive material. The occurrence of macrophytes has positive effects on richness of microorganisms (Wang et al. 2016). Yovo et al. (2016) demonstrate that *T. geniculata* are able to enhance dissolved oxygen through the well-developed aerenchyma. Maximum root diameter enables it to diffuse more oxygen into the system (Longstreth and Borkhsenious 2000).

Various species of emergent macrophyte *Cyperus* excreted bactericidal exudates within rhizosphere (Alufasi et al. 2017), and evidence toward *C. articulatus* bacterial exudates has been also documented (Caselles-Osorio et al. 2017). *C. articulatus* is able to allocate oxygen in excess to the rhizospheric region and offers an efficient elimination of nitrogen (>75%). Nevertheless, the outcomes with the similar species can differ according to season and operational conditions (Shelef et al. 2013). In CWMs, microorganisms are crucial agents for biogeochemical reactions that enhance water quality during the treatment process (Mitsch and Gosselink 2007; Saunders et al. 2013). A little alteration in the diversity or community structure of the microorganisms might directly affect the treatment performance of CWMs. During the winter, the activity of microbes produces sufficient warmness to prevent the bottom films from cold. The decomposition rates of microbes become slow as temperatures drop, thus, this can be optimized by increasing the size of wetlands to accomplish the slower reaction rates.

Tian et al. (2017) reported that the bacterial diversity is negatively correlated with the organics and nutrients removal, particularly in summer season when the population size and diversity are high. Some bacterial populations are dominated by anaerobic facultative that can work actively under both anaerobic and aerobic situations with respect to unstable ecological environments. During unfavorable conditions, several microbial populations become inactive and can remain in this state for years (Hilton 1993). Faulwetter et al. (2009) reported that the specific microbial group is responsible for the removal of particular contaminant. Hence, expanding the understanding about the organization of microorganism's community is useful to disclose the contaminants removal mechanisms in CWMs. Most common anthropogenic wastewater contaminants and their effects on human and aquatic organisms are given in Table 14.1.

14.5 Enzyme Activity

The action of enzymes within CWMs has been observed as a key indicator towards the role of microbial populations involved in wastewater treatment (Mentzer et al. 2006; Zhang et al. 2011a, b). The community structure of microbial populations has been correlated to specific enzyme activities (Zhang et al. 2006). Enzyme activity within soil substrate of a CWM (Kang et al. 1998; Martens et al. 1992) is considered as a significant factor for improving water quality (Freeman et al. 1997; Shackle et al. 2000). Functions of several enzymes within CWMs get influenced by various aspects such as biological factors (fauna, higher taxa and microbial communities), edaphic factors (nutrient composition, texture, pH, depth, organic matter content, etc.) and environmental factors (Zaman et al. 1999; Duarte et al. 2008; Reboreda and Caçador 2008).

The activity of enzymes might be altered by modifying the carbon supply either qualitatively or quantitatively to enhance the removal efficiency of CWMs (Shackle et al. 2000). They also described that supply of exogenous enzymes can improve the biodegradation processes. The actions of numerous enzymes including urease, phosphatase, protease and cellulase exhibited great dissimilarities over time. It is stated that the activity of urease was always advanced in CWMs developed with *Phragmites australis* as compared to other wetlands planted with several macrophytes. Activity of enzymes is inversely proportional to depth of soil (Aon and Colaneri 2001; Niemi et al. 2005) with maximum in the upper layer of soil substrate nearly for all wetlands. Root activity within rhizosphere presented a stronger association with enzyme activity.

Table 14.1 Most common anthropogenic wastewater contaminants and their effects on human and aquatic organisms

S. No.	Category	Contaminant	Effects	Reference
1	Organic	Nitrogen	Algal blooms in water bodies, possibly increased cancer risk, encourage infectious microorganisms such as *Pfiesteria* that can cause irritation to eye and methemoglobinemia (blue-baby syndrome) in babies	Bojcevska and Tonderski (2007)
		Phosphorus	Eutrophication, headache, gastrointestinal illnesses	
2	Heavy metals	Zn	Acidification of water, skin irritations, stomach contractions, vomiting, nausea, anemia, damage to pancreas, disturbance in protein metabolic rate, respiratory maladies, prone to infants and unborn	Calheiros et al. (2009a)
3		Pb	Kidney damage, anemia and interference with hemoglobin synthesis	Calheiros et al. (2009b)
4		Hg	Toxic to aquatic organisms like fishe, neurotoxic	Calheiros et al. (2010)
5		Cd	Temporary reduction in growth of fishe by larval mortality, in animals interacts with calcium metabolism	Truu et al. (2005)
6		Cr	Fish are more susceptible to infection, damaging the tissues of a number of invertebrates such as worms and snails	Calheiros et al. (2017)
7	Hydrocarbons	Petroleum hydrocarbons	Can damage liver and kidney severely, reproductive cytotoxicity and juvenile cancers	Calheiros et al. (2009a)
8	Microorganisms	Harmful bacteria	Several water-borne diseases	Calheiros et al. (2008a)
9		Viruses	Viral infections	
10		Protozoans	Amoebiasis, Trypanosomiasis, Diarrhea, Leishmaniasis, Trichomoniasis, Lambliasis, Toxoplasmosis and Malaria	

(continued)

Table 14.1 (continued)

S. No.	Category	Contaminant	Effects	Reference
11	Persistent organic pollutants	PCBs	Act as endocrine disrupting substances	Calheiros et al. (2008b)
12		Phthalates (plastics)	Early sexual maturation, lower orientation and attentiveness in girls, lung disorders, menace of diabetes, endometriosis and disorder in normal body functions	Calheiros et al. (2014)
13		Bisphenol A (BPA)	Lead to infertility, affect puberty and ovulation, can cause type-2 diabetes by insulin resistance, heart disease, inhibit the development of brain at gestation and enhance the risk all types of cancers	Carballeira et al. (2017)
14		Polycyclic aromatic hydrocarbons (PAHs)	Inhibits the normal working of the body. Prone to immunotoxicity, genotoxicity and embryotoxicity	Carvalho et al. (2012)
15	Emerging pollutants	Pharmaceutical products	Reduction in growth of aquatic organisms, affecting the reproductive rates of fish by masculinization	Caselles-Osorio et al. (2011)

Due to this stronger correlation, the activity of enzymes can get affected by macrophytes root activity that significantly affects the pollutants removal efficiency (Kong et al. 2009). Macrophytes can also impact soil enzyme activity via altering species composition and diversity of microbes through excreting exogenous enzymes and liberating oxygen and exudates. They are also taking part in reactivation of free enzymes that possibly get deactivated and conserved by tannin compound with several other substances in anaerobic region, through oxygenation via intensifying root structure (Neori et al. 2000).

14.6 Effect of Temperature on Microbial Activity

Numerous biogeochemical reactions that regulate the pollutants removal efficiency are greatly affected by temperature, consequently altering the overall performance of CWMs (Lee et al. 2009). Various environmental aspects showed annual cycles that facilitate the performance of whole system. Out of which, temperature of wastewater is most significant. Atmospheric effects, such as rain, water reaeration and evapotranspiration also follow seasonal patterns (Kadlec 1995). Several distinct wetland processes, for example, microbially mediated reactions and decomposition of organic matter are greatly inhibited by temperature. It also has significant influence on nitrogen transforming processes such as nitrification, mineralization and denitrification.

The reactions for phosphorus sorption have lower temperature effect. The removal of nitrogen, phosphorus and particulate carbon by physical processes are not much affected by temperature. The water and temperature of surface soil within wetland system characteristically show both annual and diurnal cycles (Tanner and Headley 2011). The diurnal variations in wastewater temperature are around 5 °C for free water surface wetlands system (Kadlec and Reddy 2001). During warm periods, the average daily wastewater temperature is almost equivalent to the average daily air temperature (García et al. 2003).

14.7 Effect of DO on Microbial Activity

The oxygen limited conditions favor methanogenesis and bacterial groups existing in humid and hot atmospheres, and consume more oxygen than it diffuses from atmosphere (Hamilton et al. 1995). Therefore, CWMs are the perfect models for fermentation process with anaerobic conditions allowing easier breakdown of organics. The metabolic action of microbes in the rhizospheric region gets influenced by the availability of oxygen (Chen et al. 2011; Saxena et al. 2019). The pH of wastewater in CWMs exerts a strong effect towards various reactions and processes, together with biological conversion, separating ionized and unionized acids and bases, cation exchange and solvability of gases and solids (Niveditha 2019).

14.8 Conclusion

One of the major characteristics of CWMs is that their roles are measured primarily by microbial population and their associated metabolic rate. The microbial biomass is the main reducer for majority of organics and nutrients. The activity of enzymes within CWMs has been observed as a key indicator towards role of microbial community in removing contaminants during the treatment process. The aerobic region of CWMs is characterized by presence of *Nitrosomonas* and *Pseudomonas aeruginosa spp.* It is also reported that the population of ammonia-oxidizing bacteria mainly *Nitrosospira sp.* is higher in CWMs designed to treat domestic wastewater as compared to other bacteria studied. The presence of these bacterial populations inside a treatment wetland has a major effect on its stability. Microbial cells attached with substratum develop biofilms that are habitually present inside a self-produced medium of extracellular polymeric substance (EPS). Microbial population use organics as nutrients and expel vitamins and several metabolites to encourage growth of additional microbes that is known as rhizosphere effect. Rhizospheric region has diverse elements that comprises minerals, organic acids, sugars, vitamins, polysaccharides, phenol and various other carbon-based materials that encourage the microbial groups to degrade organic pollutants.

The presence of macrophytes has encouraging effects on richness and community arrangement of microorganisms. Several organic materials expelled by the macrophytes in the root zone alter the microbial population dynamics. The pH of wastewater in CWMs has a strong effect toward various reactions and processes. The decomposition rates of microbes become slow as temperatures drop, thus, this can be optimized by increasing the size of wetlands to accomplish the slower reaction rates. A little alteration in the diversity or community structure of the microorganisms might directly affect the overall treatment performance of CWMs. Hence, expanding the knowledge about the organization of microbial community structure is instrumental in understanding about the contaminants removal mechanisms of CWMs.

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Chapter 15
Agricultural Waste: Its Impact on Environment and Management Approaches

Sutanu Maji, Deepa H. Dwivedi, Namrta Singh, Sachin Kishor, and Munni Gond

Abstract Waste materials are either usable or unusable products left behind after production or formulation of the main products produced by the human activities. According to the Press Information Bureau, India generates 62 million tonnes of waste (mixed waste containing both recyclable and nonrecyclable waste) every year, with an average annual growth rate of 4%. The agriculture sector is also contributing a large part through on field or off field activities. These waste materials consist of both usable and non-usable. Waste materials are of different kinds and come from various sources. The waste materials also have good nutritional values and thus, potential for its economics. The various forms, sources, and how the waste materials can be converted to many usable forms are studied and discussed here in this chapter. This chapter presented that there are solid and liquid types of waste which includes organics, dry, and biomedical wastes. The biodegradable wastes are being focused for utilizing its nutritional and desirable qualities and made into various usable products. Waste as in general is causing environmental pollution on earth surface, water, and air. Before their contamination it should be converted to usable form to minimize the pollution level as well as helps to generate employment and to make eco-friendly environment. Among the various sources agricultural crop residues, used pesticides, insecticides, fertilizers, and other indiscriminate use of chemicals causing environmental threats and already translocated through food chain causing several human diseases. The chapter also discussed the conversation of these wastes into valuable products with some tables and relevant information.

Keywords Agricultural waste · Environmental impact · Human activities · Management approaches

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15.1 Introduction

Waste materials are either usable or unusable products left behind after production or formulation of the main products produced by the human activities. A part of waste materials which is totally unsuitable for use is known as spoiled product. Economic development and rising living standards especially in the developing states have led to increase in the quantity and complexity of generated waste. Generally, waste is of two types: both hazardous and nonhazardous. The wastes are of major concern to keep the environment protected and thus, this part is generally not targeted for reuse. The nonhazardous waste has the potential to be used in many forms with little or no threat to environment and human health. Industrial diversification produces substantial quantities of industrial waste including biomedical waste which have severe environmental and human health consequences. There are several sources of waste generation including the home we reside in, besides public places, agricultural fields, hospitals, industry, etc.

India is the second largest population in the world after China with more than 1.27 billion people (17.6% of world's total population), however, it occupies only 5% of world's area (3,185,263 km^2). Sixty-eight percent of total Indian population lives in rural areas, while 32% lives in urban areas (World Bank 2014). Developing countries like India is in industrialization phase, which is an essential part to build modern society and contribute to urbanization. India is one of the fastest growing economies in the world with 7.30% GDP and expected to 10% GDP in 2030. Higher GDP is directly correlated to improved living standards. At the same time overpopulation, rapid industrialization, uncontrolled urbanization, and improved living standards produce more waste also (Nandan et al. 2017).

According to the Press Information Bureau, India generates 62 million tonnes of waste (both recyclable and nonrecyclable) every year, with an average annual growth rate of 4% (PIB 2016). The waste can be divided into three major categories: (1) organic (all kinds of biodegradable waste), (2) dry (or recyclable waste), and (3) biomedical (or sanitary and hazardous waste). Currently, 1,27,486 tonnes of municipal solid waste is being generated daily due to various household activities, other commercial and institutional activities (CPCB 2012). Among the various source municipal wastes, certain industrial waste and agriculture waste have comparatively significant impact on environment and few are extremely dangerous to the living organisms including human beings (Misra and Pandey 2005). These may pollute groundwater quality and cause air pollution by emission of greenhouse gases. With the fastest advancement of telecommunication and electronics industry e-waste and nuclear waste also need attention to solve the problem with solid waste management. A study on the wastes, their sources, nature, and effect is important to manage the waste to protect environment as well as human health.

15.1.1 Scenario of Waste Collection in India

Waste collection is much greater in metropolitan cities or other urban areas as compared to that of rural areas. Many local government bodies along with specific NGOs are involved in collecting these wastes as shown in Table 15.1.

15.1.2 Types of Waste

The principal sources of solid waste are residential households while, agricultural, commercial, construction, industrial, and institutional sectors also play an important role. A breakdown of solid waste types and sources is provided in Table 15.2. There are four major categories of waste: municipal solid waste, industrial waste, agricultural waste, and hazardous waste which are discussed in Table 15.2.

15.1.3 Classification of Waste

15.1.3.1 According to Physical Condition (Properties)

According to the physical properties, the waste is of mainly two types.

Solid Waste

Solid waste is the unwanted or useless solid materials generated from human activities in residential, industrial, or commercial areas. It may be categorized in three ways. According to its:

- Origin (domestic, industrial, commercial, construction, or institutional).
- Contents (organic material, glass, metal, plastic paper, etc.).
- Hazard potential (toxic, nontoxic, flammable, radioactive, infectious, etc.).

Liquid Waste

Liquid waste can be defined as wastewater, fats, oils or grease (FOG), used oil, liquids, solids, gases, or sludges and hazardous household liquids. These liquids are hazardous or potentially harmful to human health or the environment. They can also be discarded commercial products classified as “Liquid Industrial Waste” such as cleaning fluids or pesticides, or the by-products of manufacturing processes. There are general regulatory requirements relating to waste and additional regulations

Table 15.1 State-wise solid waste generation in urban areas, as on November 2017

S. No.	State/Union territories	Total waste generation (MT/D)	Total waste generation in (Lakh Mt./Annum)
1.	Andhra Pradesh	6525	23.82
2.	Andaman & Nicobar Islands	115	0.42
3.	Arunachal Pradesh	181	0.66
4.	Assam	1134	4.14
5.	Bihar	1192	4.35
6.	Chandigarh UT	340	1.24
7.	Chhattisgarh	1959	7.15
8.	Daman & Diu	23	0.08
9.	Dadar & Nagar Haveli	58	0.21
10.	NCT or Delhi	10,500	38.33
11.	Goa	240	0.88
12.	Gujarat	10,145	37.03
13.	Haryana	4514	37.03
14.	Himachal Pradesh	324	1.25
15.	Jammu & Kashmir	1792	6.54
16.	Jharkhand	2451	8.95
17.	Karnataka	10,000	36.50
18.	Kerala	1576	5.75
19.	Madhya Pradesh	6424	23.45
20.	Maharashtra	22,570	82.38
21.	Manipur	176	0.64
22.	Meghalaya	268	0.98
23.	Mizoram	201	0.73
24.	Nagaland	342	1.25
25.	Odisha	2460	8.98
26.	Puducherry UT	495	1.81
27.	Punjab	4100	14.97
28.	Rajasthan	6500	23.73
29.	Sikkim	89	0.32
30.	Tamil Nadu	15,547	56.75
31.	Telangana	7371	26.90
32.	Tripura	421	1.54
33.	Uttar Pradesh	15,500	56.58
34.	Uttarakhand	1400	5.11
35.	West Bengal	8675	31.66
Total		**1,45,626**	**531.53**

MT Million tonnes, *D* Day
Source: Government of India Ministry of New and Renewable Energy, 2017

Table 15.2 Sources and types of solid wastes

S. No.	Source	Typical waste generation	Types of solid wastes
1.	Residential	Single and multifamily dwellings	Food wastes, paper, cardboard, plastics, textiles, leather, yard wastes, wood, glass, metals, ashes, special wastes (e.g., bulky items, consumer electronics, white goods, batteries, oil, tires), and household hazardous wastes
2.	Industrial	Light and heavy manufacturing, fabrication, construction sites, power and chemical plants	Housekeeping wastes, packaging, food wastes, construction and demolition materials, hazardous wastes, ashes, special wastes
3.	Commercial	Stores, hotels, restaurants, markets, office buildings, etc.	Paper, cardboard, plastics, wood, food wastes, glass, metals, special wastes, hazardous wastes
4.	Institutional	Schools, hospitals, prisons, government centers	Same as commercial
5.	Construction and demolition	New construction sites, road repair, renovation sites, demolition of buildings	Wood, steel, concrete, dirt, etc.
6.	Municipal services	Street cleaning, landscaping, parks, beaches, other recreational areas, water, and wastewater treatment plants	Street sweepings, landscape and tree trimmings, general wastes from parks, beaches, and other recreational areas, sludge
7.	Process	Heavy and light manufacturing, refineries, chemical plants, power plants, mineral extraction and processing	Industrial process wastes, scrap materials, off specification products, slag, tailings
8.	Medical waste	Hospitals, nursing homes, clinics	Infectious waste (bandages, gloves, cultures, swabs, blood and body fluids), hazardous waste (sharps, instruments, chemicals), radioactive waste from cancer therapies, pharmaceutical waste
9.	Agriculture and food processing industry wastes	Crops, orchards, vineyards, dairies, feedlots, farms	Spoiled food wastes, agricultural wastes, hazardous wastes (e.g., pesticides), pulp, fruit peel, seed
10.	Mining	Open-cast mining, underground mining	Mainly inert materials such as ash

Source: Adapted from What a Waste (2012) and https://www.unescap.org/sites/default/files/CH08.PDF apply to generating, storing, transporting, treating, and disposing of hazardous and liquid wastes.

15.1.3.2 According to Their Properties

Biodegradable Wastes

Biodegradable wastes are natural organic compounds which are degraded or decomposed by biological or microbial action. Biodegradable wastes are mainly generated in food processing units, cotton mills, paper mills, sugar mills, textile factories, and sewage. Waste of slaughterhouses is biodegradable and some part of it is usable (for example, skin is used to make leather). Most of the wastes from these industries are reused. When these wastes are in excess, they are not easily decomposed and may act as pollutants (Shrama and Dwivedi 2018).

Non-biodegradable Wastes

These are not decomposed by microbes but are oxidized and dissociated automatically. Coal stone, metal scraps, sludge are generated from colliery operations. Refineries produce inert dry solids and varieties of sludge containing oil. Fly ash is the major solid waste from thermal power plants. Recently fly ash has been used to make different products for use in construction, road, etc. Generally, these wastes are not reused and accumulate in the ecosystem**.**

15.1.3.3 According to Their Effect on Human Health and Environment

Hazardous Waste

Mostly chemical, biological, explosive, or radioactive wastes, which are highly toxic and reactive, having a negative effect on human, animals, and plants, are called hazardous. Hazardous wastes, when improperly handled, can cause substantial harm to human health as well as the environment. Hazardous wastes may be solids, liquids, sludges, or gases.

Nonhazardous

Nonhazardous wastes are generally used safely and have no corrosive, reactive, toxic properties. The huge amount of nonhazardous waste creates a disposal problem, but may be converted to other product.

15.1.3.4 According to Their Origin

Nuclear Waste

Wastes from nuclear reactor are highly dangerous and requires proper management and disposal. Carbon-14, uranium-238, uranium-239 and radium-226, thorium, and plutonium are the main nuclear wastes. Two sources of nuclear waste:

Natural source: Cosmic rays from outer space with increasing altitude and latitude and emission from earth crust.

Manmade: Mining and processing of radioactive ores used in nuclear power plant, radioactive isotopes used in medicinal and industrial applications and nuclear weapons.

Thermal Waste

Thermal waste refers to the release of heat into any of the segment of environment and this type of pollution is called as thermal or heat pollution. Nuclear power plants, coal-fired power plants, nutrient effluents, domestic sewage, and hydroelectric power are the main sources of thermal waste. It degrades the water quality by changing the ambient water temperature which decreases oxygen supply and affects ecosystem composition.

Plastic Waste

Plastics are typically polymers of higher molecular mass containing other substances to improve performance and reduce cost. Monomers of plastic are either natural or synthetic organic compounds mainly generated through petroleum and natural gas industry.

There are two types of plastic waste:

Thermoplastic: which are softened by heat and can be molded (injection molded, blow molded, or vacuum formed). Good examples are acrylic, polypropylene, polystyrene, polyethylene, and PVC.

Thermosets: which are formed by heat process but are then set (like concrete) and cannot change shape by reheating. Good examples are melamine (kitchen worktops) Bakelite (black saucepan handles), polyesters, and epoxy resins.

Biomedical Waste

Solid or liquid wastes including containers, intermediate, or end products generated during diagnosis, treatment, pathological tests, and research activities of medical sciences, i.e., medicine bottles, expired medicines, syringes, medical instrument such as scissors, blades, etc.

E-Waste

E-waste or electronic waste is created when an electronic product is discarded after the end of its useful life. The rapid expansion of technology means that a very large amount of e-waste is created every minute. Electronic waste or e-waste may be defined as discarded computers, office electronic equipment, entertainment device electronics, mobile phones, television sets, and refrigerators.

15.1.3.5 According to Reuse of Wastes

Reusable/Recyclable Waste

Recycling is processing used waste into new, useful products. This is done to reduce the use of raw materials that would have been used. Waste that can be potentially recycled is termed recyclable waste. Animal product (milk, urine, and animal-dung), agriculture product (crop residue, vegetable residue, fruit residue, and fertilizers bags), plastics (grocery shopping bags, plastics bottles), glass product (wine and beer bottles, broken glass), paper products (used envelopes, newspaper, cardboard boxes, and magazines) can be reused.

Nonreusable Waste

Nonreusable/recycled waste is solid waste which are not processed nor reclaimed by a waste management system or already sorted out. The disposal of these materials is a rising concern in many parts of the developed world where environment alertness has been a rising trend.

15.2 Agriculture Waste

15.2.1 Definition

Agricultural waste is defined as the residue from the growing and processing of raw agricultural and allied products such as fruits, vegetables, meat, poultry, dairy, fishery, and crops. They are the nonproduct outputs of production and processing of agricultural products that may contain material that can benefit man but whose economic values are less than the cost of collection, transportation, and processing for beneficial/safe use. It is also called as agro-waste comprising of animal waste (manure, animal carcasses), food processing waste (only 20% of maize is canned and 80% is waste), crop waste (corn stalks, sugarcane bagasse, drops, and culls from fruits and vegetables, prunings) and hazardous and toxic agricultural waste

Table 15.3 Composition of agriculture crop residue waste

	Percent by weight (dry basis)					
Component	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Ash
Wheat straw	48.5	5.5	39.9	0.3	0.1	5.7
Rice straw	29.2	5.1	35.8	0.6	0.1	19.2
Rice husk	38.5	5.7	39.8	0.5	<0.01	15.5
Had wood	50.8	6.4	41.5	0.4	<0.01	0.9
Soft wood	52.9	6.3	39.7	0.1	<0.01	1.0
Corn cob	46.2	7.6	42.3	1.2	0.3	2.4
Cotton stalk	45.3	5.6	45.3	0.5	<0.01	3.3
Anthracite coal	78.8	2.3	2.5	0.9	0.5	13

Source: International Environmental Technology Center

(pesticides, insecticides, herbicides, etc.). Expanding agricultural production has naturally resulted in increased quantities of livestock waste, agricultural crop residues, and agro-industrial by-products. There is likely to be a significant increase in agricultural wastes globally if developing countries continue to intensify farming systems. It is estimated that about 998 million tonnes of agricultural waste is produced yearly (Agamuthu 2009). Organic wastes can amount up to 80% of the total solid wastes generated in any farm (Brown and Root Environmental Consultancy Group 1997) of which manure production can amount up to 5.27 kg/day/1000 kg live weight, on a wet weight basis (Overcash 1973).

15.2.2 Types of Agriculture Waste

Agricultural waste may be on (A) field as crop residues or (B) from agro-based industries. Agricultural crop residues on field like stem, stalks, seeds, weeds, etc. and residue after processing like husk, roots, seeds, bagasse, molasses, etc. The wastes from agro-based industries include fruit peels, pulp, cakes (oil), coir, nuts, etc.

15.2.2.1 Agriculture Crop Residues

The agricultural crop residues are materials left in an agricultural field or orchard after harvesting. The residue can be ploughed directly into the ground or converted into compost. Good management of field residues can increase efficiency of irrigation, control of erosion, improve soil aeration, and soil health (Table 15.3).

Organic Composting from Crop Residue

The crop residues focus on the equivalent fertilizer cost of the nutrients within. Although crop residues contain both macro- and micro nutrients, although values only for the macronutrients nitrogen, phosphorus, potassium, and sulfur are economically significant.

Importance of Crop Residue

Biofuel Production from Crop Residue

Because of the high carbohydrate content, crop residues can be considered as an appropriate feedstock to produce biofuels. Some algorithms have been developed to estimate the potential capacity of biofuel production from agricultural residues. Based on the experimental data obtained from a study that used ethanol organosolv pretreated rice straw to produce biohydrogen using *Enterobacter aerogenes*, the annual global amount of collectable rice straw (not total produced straw) for biofuel production was estimated about 249 million tonnes, that could approximately produce 355.78 kilotonnes of hydrogen and 11.32 million tonnes of lignin by the proposed organosolv technology and it was found that China contributes to about 32% of global potential capacity to produce biohydrogen from rice straw (Asadi and Zilouei 2017).

Mineralization Through Crop Residue

Nutrients in most crop residue are not immediately available for crop use. Their release (called mineralization) occurs over a period of years. The biological processes involved in soil nutrient cycles are complex. As a rough guide, cereal straw releases about 10–15% of its nutrients and pea residues release about 35% of their nutrients by the next year. The speed of mineralization depends on the nitrogen and lignin (fiber) content, soil moisture, temperature, and degree of mixing with the soil. N is released fairly quickly from residue when the content is higher than 1.5% (such as in pea residues). In contrast, below 1.2% (such as cereal residue), soil-available N is fixed (called immobilization) by the microbes as they decompose the residue (Table 15.4).

Thus, pea residue would have short- and long-term benefits to soil fertility, whereas cereal straw would reduce next year's soil supply of available nutrients. Over time, the nutrients fixed by soil microbes and humus are released and available to crops. Nutrients from residue are not fully recovered by crops. Just like fertilizer nutrients, nutrients released from crop residue into the soil are susceptible to losses such as leaching (N and S), denitrification (N), immobilization (N, P, K and S), and fixation (P and K).

Efficiency of Nutrient Uptake

The efficiency of nutrient uptake by crops from fertilizers or residue release is generally thought to be similar. For example, there is about 50% recovery of N in the above-ground plant in the first year. There is some residual benefit of fertilizers as the crops take up a small amount of the nutrients 2 and 3 years later. Fertilizer placement can significantly affect the efficiency of crop uptake. The impact of residue placement (buried by tillage or left on the surface in zero tillage) on nutrient cycling and efficiency is under study.

Composition of Crop Residue Waste

The composition of crop residue waste largely depends on the nature of crop plants as shown in Table 15.5.

15.2.2.2 Waste from Agricultural Livestock

Animal wastes are commonly considered the excreted materials from live animals. However, under certain production conditions, the waste may also include straw, hay, wood shavings, or other sources of organic debris. Application of excreta to soil brings benefits such as improved soil tilth, increased water-holding capacity, and some plant nutrients. Concentrated forms of excreta or high application rates to soils without proper management may lead to high salt concentrations in the soil and cause serious on- or off-site pollution. Animal waste contains many beneficial constituents that if recycled effectively, can be used as fertilizer for crops, fodder for animals, and to produce energy. Animal manure is rich in nitrogen, phosphorus, and potassium. In addition to providing supplemental nutrients for crop growth, manure has several beneficial effects on soil properties (Table 15.6). Application of organic waste decreases the bulk density of the soil by increasing both the organic fraction of the soil and the stability of aggregates (Mondal 2008).

The most common environment concern with animal wastes is that it affects the atmospheric air with offensive odors, release of large quantities of CO and ammonia which might contribute to acid rain and the greenhouse effect. It could also pollute water sources and be instrumental in spreading infectious diseases. If the disposal of water is not properly planned it might create social tension owing to the release of odors and contamination of water sources. Proper disposal and returning of nutrients back in the soil without pollution and spreading of diseases/pathogens, is required for efficient utilization of wastes on large farms (Mondal 2008).

Table 15.4 Composition of agriculture waste

Agriculture waste	Chemical composition (% w/w)						References
	Cellulose	Hemicellulose	Lignin	Ash (%)	Total solid (%)	Moisture (%)	
Sugarcane bagasse	30.2	56.7	13.4	1.9	91.66	4.8	El-Tayeb et al. (2012), Nigam et al. (2009)
Rice straw	29.2	23.5	36.1	12.4	98.62	6.58	El-Tayeb et al. (2012)
Corn stalks	61.2	19.3	6.9	10.8	97.78	6.40	El-Tayeb et al. (2012)
Sawdust	45.1	28.1	24.2	1.2	98.54	1.12	El-Tayeb et al. (2012), Martin et al. (2007)
Sugar beet waste	26.3	18.5	2.5	4.8	87.5	12.4	El-Tayeb et al. (2012)
Barley straw	33.8	21.9	13.8	11	–	–	Nigam et al. (2009)
Cotton stalks	58.5	14.4	21.5	9.8	–	7.45	Nigam et al. (2009)
Oat straw	29.4	27.1	17.5	8	–	–	Martin et al. (2007)
Soya stalks	34.5	24.8	19.8	10.3	–	11.84	Motte et al. (2013)
Sunflower stalks	42.1	29.7	13.4	11.7	–	–	Motte et al. (2013)
Wheat straw	32.9	24.8	8.9	6.7	95.6	7.0	Nigam (2001), Nigam et al. (2009), Martin et al. (2007)

Types of Livestock Waste

Solid Waste

Waste containing 20% or more solids or with moisture content of 50% MWB or less is considered to be solid waste. Solid wastes are treated by drying or composting. Dried wastes are used not only as fertilizer but also as fuel for combustion to obtain energy (Haga 1998).

Slurry

Slurry is a type of liquid manure that can be used on fields as fertilizer. If the soil or plants are unable to absorb the slurry or if the slurry is spread in too high a concentration, the run-off can get into water systems. Slurry is generally more polluting than raw sewage. When slurry tanks are accidentally or deliberately breached large amounts of slurry can spill into rivers, streams, or lakes, including wetlands causing severe environmental problems. Many incidents are not reported. Animal waste is found in soil, surface water and groundwater, and sea water. Slurry disturbs aquatic

Table 15.5 Cellulose content and composition [% (w/w) of dry matter] of agriculture waste

Agriculture waste	Cellulose (%)	Hemicelluloses (%)	Lignin (%)
Hard wood	40–50	24–40	18–25
Soft wood	40–50	25–35	25–35
Nut shells	25–30	25–30	30–40
Corn cob	45	35	15
Grasses	25–40	35–40	10–30
Wheat straw	33–40	20–25	15–20
Rice straw	40	18	5.5
Leaves	15–20	80–85	–
Switch grass	30–50	10–40	5–20
Solid cattle manure	1.6–4.7	1.4–3.3	2.7–5.7
Primary waste water solids	8–15	–	24–29
Paper	85–99	–	0–15
News paper	40–55	25–40	1830
Hardwood stem	40–50	24–40	18–25
Peanut shell	22.1	12.1	35.2
Rice hull	49.1	9.6	12.9
Sugarcane leaf and stalk	40	29	13
Sorghum leaf and stalk	31	30	11

Source: Sindhu (2015); Dueñas et al. (1995); Martin et al. (2007)

ecosystems by increasing nitrogen and phosphorus levels leading to the growth of toxic algae, which poison the fish and it decreases oxygen levels causing fish to suffocate (Table 15.7).

Importance of Agro-Livestock Waste

Livestock and poultry industries produce meat, milk, and egg, and also generate large volumes of waste water and solid wastes that could be beneficial or harmful to the environment. The waste products which include livestock or poultry excreta and associated feed losses, beddings, washwater, and other such waste materials represent a valuable resource that if used wisely, can replace significant amounts of inorganic fertilizers.

Animal waste contains many beneficial constituents that if recycled effectively, can be used as fertilizer for crops, fodder for animals, and to produce energy. Animal manure is rich in nitrogen, phosphorus, and potassium. In addition to providing supplemental nutrients for crop growth, manure has several beneficial effects on soil properties. Organic manure decreases the bulk density of the soil and also improves both organic fraction and stability of the soil. Organic manure also increases rate of water infiltration, water-holding capacity, and electrical conductivity of the soil.

15.2.2.3 Agro-Industry Waste

Waste from Fruit and Vegetable

Fruits and vegetables are the most utilized commodities among all horticultural crops. They are consumed raw, minimally processed, as well as processed, due to their nutrients and health-promoting compounds. With the growing population and changing diet habits, the production and processing of horticultural crops, especially fruits and vegetables, have increased very significantly to fulfill the increasing demands. The significant amount of fruits produced globally include 124.73 million metric tons (MMT) of citrus, 114.08 MMT of bananas, 84.63 MMT of apples, 74.49 MMT of grapes, 45.22 MMT of mangoes, mangosteen, and guavas, and 25.43 MMT of pineapples. Production of some vegetables include potato (3820.00 MMT), tomatoes (171.00 MMT), cabbages and other brassicas (71.77 MMT), carrots and turnips (38.83 MMT), cauliflower and broccoli (24.17 MMT), and peas (17.42 MMT) (FAO 2017).

Higher production and growth, and the lack of proper handling methods and infrastructure, have led to huge losses and waste of these important food commodities, as well as their components and by-products and residues. The United Nations has estimated that at least one-third of the food produced in the world (estimated as 1.3 billion metric tons) is lost and wasted every year (FAO 2014) and losses and waste of horticultural commodities are the highest among all types of foods, reaching up to 60% (Table 15.8).

Agricultural Waste Generation

As noted earlier, agricultural development is usually accompanied by wastes from the irrational application of intensive farming methods and the abuse of chemicals used in cultivation, remarkably affecting rural environments in particular and the

Table 15.6 Composition of oil cake

Oil cakes	Dry matter	Crude protein	Crude fiber	Ash	Calcium	Phosphorus	References
CaOC	90.0	33.9	9.7	6.2	0.79	1.06	Ewing (1997)
COC	88.8	25.2	10.8	6.0	0.08	0.67	Gohl (1970)
CSC	94.3	40.3	15.7	6.8	0.31	0.11	Friesecke (1970)
GOC	92.6	49.5	5.3	4.5	0.11	0.75	Kuo (1967)
MOC	89.8	38.5	3.5	9.9	0.05	1.11	Kuo (1967)
OOC	85.2	6.3	40.0	4.2	–	–	Maymone et al. (1961)
PKC	90.8	18.6	37.0	4.5	0.31	0.85	Owusu et al. (1970)
SuOC	91.0	34.1	13.2	6.6	0.30	1.30	Owusu et al. (1970)

CaOC Canola oil cake, *COC* Coconut oil cake, *CSC* Cotton seed cake, *GOC* Groundnut oil cake, *MOC* mustard oil cake, *OOC* Olive oil cake, *PKC* Palm kernel cake, *SuOC* Sunflower oil cake global environmental in general. The waste generated is dependent on the type of agricultural activities carried out.

15.3 Impact of Agricultural Waste

Environment is everything that is around us. It can be living or non-living things. It includes physical, chemical and other natural forces. Living things live in their environment. They constantly interact with it and adapt themselves to conditions in their environment. In the environment there are different interactions between animals, plants, Insects, soil, water, and other living and nonliving things (Wikipedia 2018a). Agriculture is the cultivation of land and breeding of animals and plants to provide food, fiber, medicinal plants, and other products to sustain and enhance life (Anonymous 1999).

15.3.1 Soil

Soil is a mixture of organic matter, minerals, gases, liquids, and organisms that together support life. Earth's body of soil is the pedosphere, which has four important functions:

It is a medium for plant growth.
It is a means of water storage.
It is a means for supply and purification.
It is a modifier of Earth's atmosphere.
It is a habitat for organisms; all of which, in turn, modify the soil (Wikipedia 2018b).

Soil erosion and sedimentation are caused by the agriculture waste. Increased erosion rates from tilled fields can cause excessive deposition of fine sediments in receiving streams that block interstitial spaces and river-bed gravels which are

Table 15.7 Composition of agro-livestock waste

Nutrient	Poultry manure	Cow dung	Swine waste	Goat droppings
Organic carbon (%)	16.0	8.0	13.1	5.2
Nitrogen (%)	2.1	1.6	2.0	1.8
Available phosphorus (mg kg^{-1})	2.2	0.75	0.70	2.10
Organic matter (%)	28.8	13.5	24.2	10.9
Calcium (%)	6.2	4.2	6.1	3.2
Magnesium (%)	2.0	2	2.1	1.3
Potassium (%)	3.3	0.65	0.60	0.40
Sodium (%)	0.70	0.32	0.40	0.24
Carbon:nitrogen ratio	8.0	4.3	6.8	2.6

important spawning habitats for many fish species. Sediment deposition also contributes to changes in channel morphology and flow regime. Additionally, suspended sediments reduce light penetration, scour surfaces and may interfere with feeding mechanisms, drift rates and respiration of macro invertebrates and fish (Doeg and Koehn 1994; Wood and Armitage 1997; Relyea et al. 2000).

15.3.2 Environment

Pesticides that are used for the elimination of harmful insects, microorganisms, and other pests when they mix with soil, water, air, and food, cause problems on the agricultural foods and affect both human health and natural balance and so finally become an environment problem. Pesticide runoff is an important contributor to surface-water contamination (Wohlfahrt et al. 2010). Additionally fields, streams, lakes, ground water, and sea are converted to a kind of poison storage in time (Şimşek et al. 1991). There are hundreds of pesticides that are used in the world. According to WHO's classification, 33 pesticides are very dangerous, 48 of them are quite dangerous, 118 of them are moderately dangerous, and 239 of them are less dangerous of the total 700 mostly used pesticides. A 75% rate of pesticide usage belongs to developed countries. Pesticides and insecticides contaminate water. Contaminated water contains the heavy metals viz.; mercury, arsenic, lead, cadmium, etc. which affect the environment.

Table 15.8 Commercially manufactured products from fruit and vegetable wastes

Apple	Extra pomace after juice extraction used to prepare pectin, cider, vinegar, chutney
Apricot	Kernels after removing seed coat of white apricot can be added to jam to improve color and appearance. Oil from kernel and seed are used in pharmaceutical and cosmetic industry. Oil cake is used for cattle feed
Citrus	Fruit peels are utilized for making candy and oil is used in confectionery. Rages from galgal and orange are used to make pectin. Rages are utilized in making marmalade, toffee. This is also a good feed for cattle. Citric acid is produced from sludge and others residues can be fermented to make vinegar. Peel and seed oil are also used in many cosmetic industry
Grapes	Seed oil is used as cattle feed. Pomace is used in jelly, chutney, and jam making. Stem portion is used to prepare cream of tartar
Guava	Fruit cores, seeds, peels left after juice extraction is used to prepare popular product guava cheese
Mango	Stone of fruits are powdered followed by drying and utilized in many edible products. Peels are used to make vinegar by fermentation
Jackfruit	Seeds from fully ripe fruit are eaten after roasting. Pectin is extracted from rind and perigons
Tomato	Seeds are used to prepare edible oil
Pineapple	Juice from shell, trimmings, and other wastes may be used for secondary canning. Fruit core is used to prepare candy as well as used as cattle feed

15.3.3 Human Health

Water pollution creates a vicious cycle of contamination of the human food chain. Water and food are interlinked and difficult to separate. Many communicable and noncommunicable human diseases are related to water, soil geochemistry, and environmental pollution. There are numerous examples of environmental pollution leading to epidemics of serious human diseases (Kolpakova 2004; Deleanu et al. 1981). In agricultural areas, water can be contaminated with microbes, toxic heavy metals, such as lead, cadmium, or arsenic; fluoride; and various toxic agrochemicals (Wittmer et al. 2010, Belden et al. 2000 and Meyer et al. 2011). According to Gadde et al. (2009), open burning of crop stubble results in the emissions of harmful chemicals like polychlorinated dibenzo-p-dioxins, polycyclic aromatic hydrocarbons (PAH's), and polychlorinated dibenzofurans (PCDFs). Burning of crop stubble has severe adverse impacts especially for those people suffering from respiratory disease and cardiovascular disease. Pregnant women and small children are also likely to suffer from the smoke produced due to stubble burning. Inhaling of fine particulate matter of less than PM 2.5 μg triggers asthma and can even aggravate symptoms of bronchial attack (Kumar et al. 2015).

Industrial agriculture focuses on the growth of the same crop season after season. Mono crops cause nutrient loss and reduce the soil's ability to naturally eliminate pests and replenish nutrients. To compensate, industrial agriculture uses heavy doses of chemical pesticides. Likewise, factory farming is contaminating the world with industrial operations that raise massive quantities of animals (usually cows, pigs, chickens, or turkeys) in overcrowded, confined, and unsanitary conditions (Hatz 2009). The price of food is at a relatively cheap cost, but is actually a cost affecting our health in a significant way. The oldest and most well-studied agricultural respiratory diseases are from exposures to organic dusts such as grain processing and confined animal feeding operations (CAFOs), (e.g., swine confinement facilities) (Kirkhorn and Facoem 2001). Organic dust toxic syndrome (ODTS) is common and may be seen in up to 34% of CAFO workers (Von Essen and Donham 1999).

15.4 Conversion and Utilization of Agricultural Waste

Agricultural wastes are basically unusable substances which may be either liquid or solid produced as result of cultivation processes such as fertilizers, pesticides, crop residues, and animal waste. Agricultural waste management is part of the ecological cycle in which everything is cycled and recycled such that an interdependent relationship is maintained in the ecosystem. By waste management, all the plant wastes are placed at the right place and right time for the best utilization in order to convert into useful products and pollution control. Globally, 140 billion metric tons of biomass is generated every year from agriculture. Ministry of New and Renewable Energy, Govt. of India estimated that about 500 Mt. of crop residue is generated every year (Shehrawat and Sindhu 2012). Agricultural waste contains biodegradable hemicellulose and cellulose materials, which on decomposition gives good nutrients to plants. Cow dung is commonly available in rural areas, which is rich in nutrients and microorganisms. Cow dung can be used as good seeding material as it is available in the agricultural farm itself from livestock. One of the main aims of the study is to reduce the overall time required for composting. Therefore, cow dung is mixed with agricultural waste as seeding agent (Kale 2000).

15.4.1 Agricultural Waste Improves Soil Fertility

Edwards and Bohlen (1996) reported that the pH range between 6 and 7 promotes the availability of plant nutrients like NPK, so vermicompost should be applied in soil. Chemical parameters like pH and electrical conductivity (EC) were determined by ISI Bulletin (Butterworth and Mosi 1986) by using digital pH and conductivity meters. Vermicompost improves the pH of soil and make available the nutrient for the crop yield reported by Srikanth et al. (2000). The deficiency in organic carbon reduces the storage capacity of soil nutrients and reduction in soil fertility reported by Kale et al. (1992). Vasanthi and Kumarasamy (1999) and Srikanth et al. (2000) reported that the incorporation of vermicompost with farm yard manure have been shown to increase organic carbon content in the soil.

Atiyeh et al. (1998) reported that the conventional compost had higher ammonium, while the vermicompost tended to be higher in nitrates, which is the more available form of nitrogen. Kale and Bano (1994) reported that the vermicompost shows the high values of NPK as high as 7.37% nitrogen (N) and 19.58% phosphorus as P_2O_5 in worm's vermicast. Lee et al. (2004) suggested that the passage of organic matter through the gut of worm results in phosphorus (P) converted to forms which are more bioavailable to plants. Suhane et al. (2008) reported that exchangeable potassium (K) was over 95% higher in vermicompost. The nutrients N and P and the intestinal mucus excreted by worms are further used by the microbes for multiplication and vigorous soil remediation and fertility improvement action reported by Teotia et al. (1950).

15.4.2 Conservation of Paddy Straw Waste Material

Paddy straw can be used as a source of energy for small-scale processing units, for carrying out various processes like washing, boiling, canning, etc. A mushroom processing unit is being run by a farmer in village Aterna of district Sonipat; his processing unit works under biomass energy. Paddy straw, cotton sticks, mustard sticks, and husk is utilized as a source of energy in the processing unit (Shehrawat and Sindhu 2012).

15.4.3 Utilization of Biogas Plant Waste

Forty-one farmers possessed biogas plant. Slurry thrown out of the biogas plant is utilized by the farmers (100.00) as manure and for composting and vermicomposting by 78.04% of farmers. This result was analogous with the findings of Ponni et al. (2007) that vermicompost can be used as manure on farm, the application of FYM + vermicompost @ 2.5 t/ha along with the panchagavya 3% proved to be the best treatment as it was found to record the highest plant height (83.17 cm), number of branches (38.23) and leaves (1115.87) and also recorded the mass herbage (44.81 g/plant).

15.4.4 Utilization of Floricultural Waste Product

After picking flowers, the whole plant is a waste along with the damaged and unsold flowers. The left out flowers are generally unsold or sold at least price. Few farmers use it in composting, vermicomposting, and green manuring, but mostly it becomes a waste. The left out flowers can be dried and used for making dry flowers which is an upcoming industry. The dry flowers can be painted, colored, and dyed and various floral products such as cards, pictures, wall hangings, arrangements, potpourris, and pomanders can be made out of them. Dilta et al. (2011) also suggested that dry flowers can be painted, colored, dyed, and sold at very high prices.

15.4.5 Conservation of Horticultural Waste Product

Horticultural crops were cultivated by 64 farmers. Damaged or spoiled fruits and vegetables, dead plants, branches, leaves, and unsold fruits and vegetables are the horticultural wastes. Among these, damaged fruits and vegetables are turned into compost/vermicompost or fed to animals by 70.31% of farmers. The dead plants, branches, and leaves were fed to animals by 100.00% and composted by 70.31% of farmers. Unsold fruits and vegetables are fed to animals by 100.00%, composted by 70.31%, and 26.56% farmers sold it after processing.

Value added products can be made from surplus fruits and vegetables and then sold in market; this will not only help the farmers avoid wastage but to earn more. Another way of preserving the unsold fruits and vegetables is drying them and then selling. Various chemicals can also be extracted from waste fruits and vegetables like citric acid, lactic acid, acetic acid, etc. Production of lactic acid was studied that it can be produced through the batch and fed batch fermentation method using hydrolyzed potato starch, results from the findings of Zhang and Mu (2011) concluded that potato residues can also be used for extraction of pectin.

15.4.6 Uses of Sugarcane Waste Product

From sugarcane crop, residues are sugarcane trash and bagasse. From the farmers those who cultivated sugarcane (43 farmers), 48.83% used the bagasse as fuel in making jaggery, 46.51% turned it into compost/vermicompost, and only 11.62% sold it to paper/cardboard industry or power plant. Farmers used sugarcane trash to feed their animals (100.00), composting/vermicomposting (46.51), sell as animal feed (16.28), and use it for mulching (1.67). Apart from composting and feeding bagasse and trash to animal, bagasse can also be used as planting for growing green fodder. Besides this, sugarcane bagasse has one more important use which is production of biogas; this is similar to the findings of Dellepiane et al. (2003) who conducted the study due to the existing difficulty of finding energy sources and reducing pollution, the use of renewable sources and highly efficient technologies for electrical energy production, the combination of these two aspects, namely, a molten carbonate fuel cell system fed with biomass-derived syngas. In particular, the biogas comes from bagasse and barbojo, the sugarcane residues. So far in developing countries they have been wasted or partly used with poorly efficient technology.

15.4.7 Conservation of Cotton Waste Material

Seventy-five farmers cultivated cotton crop. Cotton sticks which are left after the picking of cotton are used as fuel and stored by all the farmers. Cotton sticks were not utilized for any other purpose. If the farmers sell the cotton sticks to power plants, plywood industries, particle board industries they can add to their income. Another way of changing the waste cotton sticks into useful material is by chipping and converting them into compost. Cotton waste can also be used in biogas production by treating it anaerobically. This was similar to the findings of Isci and Demirer (2006), who found out that cotton wastes are a good source of biogas. Approximately, 65, 86 and 78 mL CH4 were produced in 23 days from 1 g of cotton stalks, cotton seed hull and cotton oil cake in the presence of basal medium (BM), respectively. BM supplementation had an important positive effect on the production of biogas.

15.5 Summary

Waste materials are produced by human activities and it is being used as potential source for making various products. Generally, agricultural wastes are rich in nutrients, sugars, vitamins, pigments etc. also which make them source materials instead of wastes. They are utilized as both edible and nonedible products. Agri-wastes are of solid and liquid in nature causing environmental hazards making the ecosystem unsustainable when they are lying unattended. Industrial liquid waste is polluting river water and air. With intervention of some practices these wastes may be converted to many products like bio-compost, fermented products, candy, cosmetic products, pharmaceutical products, etc. Thus, reuse of agri-wastes is the future of alternative source of raw materials for various products which not only will reduce the production cost but also reduce the pollution level and will make the planet eco-friendly.

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