Sughosh Madhav · Pardeep Singh ·
Vandana Mishra · Sirajuddin Ahmed ·
Pradeep Kumar Mishra *Editors*

# Recent Trends in Wastewater Treatment

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# Chapter 1
# Water Quality Characterization of Industrial and Municipal Wastewater, Issues, Challenges, Health Effects, and Control Techniques

**Nusrat Khanam, Aditya Abha Singh, Anil Kumar Singh, and M. K. Hamidi**

**Abstract** Water is vital, renewable resource, and crucial for supporting all life forms. Water quality is important concerning both environmental and economic aspects. Rapid urbanization, industrialization, agriculture practices increase the water pollution. Water pollution refers to the changes in any water body's chemical, physical, and biological condition owing to the input, substitution, or removal of organic, inorganic, biological, or radioactive substances, etc. Point source includes industrial and municipal wastewater in which pollutant travels directly from source to water; while non-point source includes urban and agricultural run-off which make their way into the aquatic ecosystems. Various types of industrial wastewater include suspended solids, chemicals, and toxic compounds, metals, non-metals, organic, inorganic pollutants, solvents, and solid–liquid waste. While the composition of municipal wastewater varies, but chiefly comprises substances like food matter, beverages, inorganic and organic solids, and pharmaceutical wastes, etc. There are wastewater-related challenges and issues both in developed and developing countries. While major problems are being faced by developing countries like lack of access to clean water, sanitation, effective wastewater management causing multiple diseases across the population, besides, the lack of sufficient funds. Humans face health problems that are associated with water-related infectious diseases like diarrhoea, hepatitis, cholera, dysentery, dermatophytosis, malaria, yellow fever, dengue fever, filariasis, and other disorders. Pollution prevention is the key that reduces the load of pollutants discharged into the water bodies. Pollution control strategies seek the management of pollutants by stern actions, legislation and regulations, public awareness for sustainable use of resources, and recycling and treatment of industrial and municipal wastewater. Recent technologies such as UV led-induced advanced oxidation processes, peracetic acid-based advanced oxidation processes, membrane bioreactor, electrochemical advanced oxidation processes are

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employed for removing pollutants from the wastewater, United Nations, World Health Organization, World Wide Fund for Nature, United Nation Environment Programme, are the few international organizations that work for water quality and its conservation. Moreover, in India steps undertaken for water-related issues includes Swachh Bharat Mission, Ganga action plan, the National water mission, and water quality monitoring and regulation by Central Pollution Control Board. Furthermore, we need to improve the current status of water bodies through water resource management and also need proper strategies for solving wastewater-related problems throughout the world.

**Keywords** Human health · Industrial wastewater · Municipal wastewater · Organization · Pollution · Water quality

## 1.1 Introduction

The most essential element and a unique gift for human life is water, and irreplaceable for many of its uses in supporting nonliving and living things (Singh and Singh 2021). It is one of the life-supporting elements of the ecosystem and is a symbol of social equity and justice, which provides energy to all organisms of the earth and maintains the equilibrium of the ecosystem (Li et al. 2005; Chakraborty et al. 2021). For our existence, appropriate water quality is necessary on Earth. Approximately 70% of the human body is composed of water, and a majority of the earth's fauna and flora thrive in water (Smol 2009). We require adequate clear water to decimate our thirst, agriculture field irrigation, and assist all forms of life such as plants and animals, and micro-organisms in the ecosystem. We as humans require fresh and clean water in our locality, community, industries, businesses, as well as in natural environment. Since ages, water has aided into trade, commerce, progress, and innovation (Lufkin 2017). However, these commercial advances have had environmental costs and impacts (Goyes and South 2017).

The need for clean water is essential today and is everlasting (Vigil 2003). However, it is polluted or wasted, unsafe, and unhygienic due to anthropogenic activities and pollution (Faroque and South 2021). When the physical, chemical, or biological property of any water body gets altered due to the different kinds of pollutants, it is called as water pollution (Goel 2006). Pollution of water is also a violation of access to clean water under human rights (Barlow 2010). Both groundwater and surface water are being contaminated owing to the rapid urbanization, industrialization, and agriculture practices. Different pollution and industrial waste substances affect the potability of this precious natural resource (Faroque and South 2021). Nevertheless, abundantly supplied with water, planet earth faces numerous immediate water crises due to demographic changes, overuse, and overconsumption, pollution, climate change, and poor wastewater management (Brisman et al. 2018; Leahy 2018; García Ruiz et al. 2020). Water pollution has been the main focus for scientists and government protecting our aquatic ecosystem, and its quality is important because of the serious condition of water pollution and global insufficiency of water resources (Fig. 1.1).

There are chiefly two forms of water pollution sources: point and non-point source. The emissions from point sources are the chief source of pollution in water. It includes industrial wastewater besides the municipal wastewater. Industrial wastes and sewage releases contribute a significant load of pollutants to water bodies, since they increase BOD and nutrient content, promoting destabilized ecosystem (DWAF and WRC 1995; Murray et al. 2000). Non-point sources runoff, like pesticides and fertilizers, make their way into an aquatic ecosystem. Once water is contaminated, it becomes tremendously tedious and expensive to make it clean again, which renders it unusable (Denchak 2018). The rapid increase of population doubled the gap between demand and supply of resources (Matta 2010; Juma et al. 2014). Physiochemical characteristics of water can also influence the biodiversity of the aquatic system and later can lead to an impact on the water quality (Soja and Wiejaczka 2014). Turbidity, electrical conductivity, pH, and temperature are the physical characteristics of water bodies. DO, BOD, and COD are appropriate pollution indicators that have negative impacts on water quality (Hassan and Mahmood 2018).

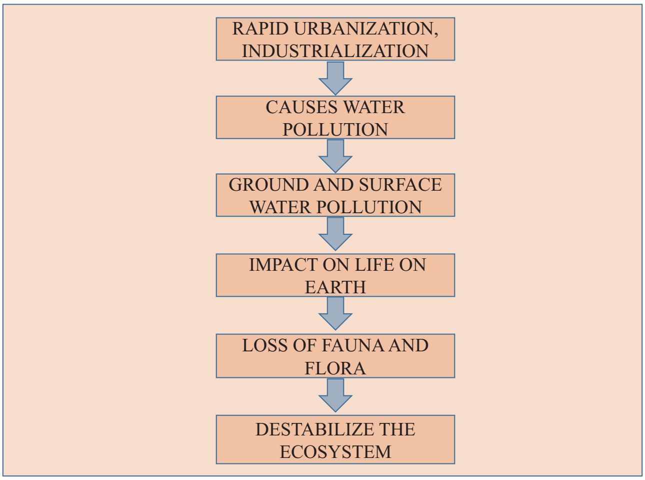

**Fig. 1.1** shows that unsustainable human activities lead to water pollution, which causes negative implications on flora, fauna, and ecosystem. (It has been referred from DWAF and WRC 1995; Murray et al. 2000; Faroque and South 2021; Smol 2009)

## 1.2 Industrial Wastewater: Sources and Composition

Water pollution in which pollutants are discharged from industries such as mining, steel industries, petroleum industry, chemical plants, pharmaceutical industry, food processing, and paper and textile mills is among the major problems encountered by India and other countries in the world (Papirio et al. 2013; Doushanov 2015; Gadipelly et al. 2018; Li et al. 2019; Singh and Chandra 2019; Varjani et al. 2020). Different industries release a variety of pollutants, including chemical compounds, toxic substances, volatile compounds, heavy metals, and radioactive substances that change the physico-chemical status of water bodies, directly and indirectly affecting all types of living organisms (Ekpo et al. 2008; Rahman et al. 2009; Verma and Dwivedi 2013). The industrial sector consumes a big quantity of water and eventually produces a huge volume of wastewater discharge that contains inorganic and organic pollutants and solid and liquid waste (Paul et al. 2012; Crini et al. 2018; Hasan et al. 2019). Microbes biodegrade the organic pollutants and modify them into a simple form that benefits the aquatic ecosystem. However, inorganic pollutants like Arsenic (As), chromium (Cr), cadmium (Cd), nickel (Ni), mercury (Hg), cobalt (Co), vanadium (V), etc. are poisonous and cannot be removed easily by microbiota. Some minerals are required at a low level for human health; however, they are toxic at higher dosages and fall into toxic inorganic pollutants type (Verma and Dwivedi 2013).

Over 700 emerging toxic waste, their metabolites, and transformed products have been listed in the European aquatic system. Some naturally occurring chemical and inorganic pollutants were identified, whose environmental impact is severe and has a more adverse impact on human health (Dulio and Slobodnik 2009; Geissen et al. 2015). These contaminations cause skin cancer, eye irritation, digestion-related disease, lung infection, and other infectious diseases. Most of the inorganic pollutants are non-biodegradable hence they persist for a long period in both fresh and saline water and accumulate in the food chain (Kesari et al. 2021). Moreover, several pharmaceutical products contain toxic compounds that disrupt the endocrine gland and their secretion in the human body (Bolong et al. 2009). Chemical industries linked with the aluminium production release a bulk of fluoride through their discharge to water bodies. Ammonia is released from different fertilizer industries, while a huge quantity of cyanide is generated from the steel plant. Chromium salts are used in the industrial process to produce chromium containing compounds and sodium dichromate. Textile industries discharge a large volume of dark-coloured pollutants that contain a high concentration of sulphate, sulphide, chloride, magnesium, and calcium (Paul et al. 2012; Madhav et al. 2018, 2021). Moreover, different hazardous inorganic chemicals are immensely used during textile wet processing and remain with processed water, which is very challenging to eliminate (Madhav et al. 2018). Mining industries require a large amount of water for operational methods such as hydrometallurgical extraction, coal washing, mineral processing, and discharge wastewater containing acidic and toxic substances (Kesieme et al. 2012). The iron and steel industry are the major industry that contributes inorganic effluent such as cyanide, sulphides, oxides of copper, chromium, cadmium and mercury, sulphate, ammonia, thiocyanate, thiosulfate, fluorides (Verma and Dwivedi 2013; Doushanov 2015; Singh and Gupta 2016). These are finally released into water bodies as emissions being harmful to human health and the aquatic life. The food processing industry includes the vegetable industry, fruit industry, dairy industry, meat and fish processing industry. These industries discharge dissolved material, suspended solids, carbohydrate, starch, pectin, fat, protein, and sugar into the environment (Kroyer 1995). Moreover, the nuclear and electric power plants, petroleum refineries, steel industries, boilers from industries eject large amounts of heat to the aquatic ecosystem leading to modifications in the chemical, biological, and physical features of the receiving water systems (Singh and Gupta 2016).

## 1.3 Municipal Wastewater: Sources and Composition

Municipal wastewater or the domestic discharge is the wastewater generated principally by the people. This type of wastewater is predominantly discharged from households, hospitals, laundries, and other sources such as commercial market places, hotels, cattle, and poultry farms, etc. (Yetilmezsoy and Sapci-Zengin 2009; Otunyo et al. 2016; Lv et al. 2018; Khan et al. 2021; Tian et al. 2021; Gustavsson et al. 2022). Its constituent varies according to the geographical location and population of the area. Municipal wastewater is the major component of water pollution (CPCB 2021a). Continuous exploitation of water resources for quenching the human needs and socio-economic development results in the production of municipal wastewater (Teodosiu et al. 2016). The municipal wastewater chiefly contains all the substances utilized by the humans such as food, beverages, pharmaceuticals, oil, fatty acid, grease, dissolved salt, microplastic and nitrogen, inorganic phosphorus pollutant, household chemicals, and substances that are released into the sewer system (Morrison et al. 2001; Kroiss 2003; Pastore et al. 2015; Koch et al. 2016; Goswami et al. 2021; Madhav et al. 2021).

Wastewater treatment methods produce sewage sludge, which is a concentrated and bioactive filtrate of organic clay-sized particles (Fei-Baffoe et al. 2014). Those area faces problems of water pollution where the wastewater treatment systems are simple or not efficient (DWAF and WRC 1995; Murray et al. 2000). The proper management of solid waste is one of the major problems the human population is facing due to different lifestyles, habits, the latest technological and scientific advancement, and the consumption of new products (Miezah et al. 2015). These factors increase both the quantity and complexity of waste generation (Fei-Baffoe et al. 2014). In India, it is estimated that roughly one lakh people produce near about 16,662 million litres of wastewater daily. Furthermore, approximately 70% of the humans near river Ganga and Yamuna have access to sewerage facilities and generate around 33% of wastewater (Bhattacharya et al. 1997). In urban areas, due to sewer connection often common point source exists which discharge multiple pollutants in the river that severely impacts its water quality (Seitzinger et al. 2010;

Hofstra et al. 2013; Lebreton et al. 2017; van Wijnen et al. 2018; Font-Palma 2019; Van Puijenbroek et al. 2019). Organic and inorganic pollutants in municipal wastewater widely vary; organic pollutants can be subdivided into toxic, persistent, and bioaccumulative substances and more polar substances such as pharmaceutical products. While, inorganic pollutant includes nano particles, micro-plastics and metals (Geissen et al. 2015). According to UNEP (2016), ammonia is the common effluent in municipal wastewater that is toxic to water biodiversity. Hospitals are an important source of pollutants due to diagnosis, research and development actions, and medicine excretion by patients, including the active component of drugs, radioactive markers, etc. especially those without appropriate treatment (Wang et al. 2020). Presently the COVID-19 pandemic is the chief and one of the biggest issues around the world. The novel SARS-CoV-2 has been expanded all over the world. It's secondary transmission via sewage is a major problem that can be increased by the faeces of patients (Teymoorian et al. 2021) (Table 1.1).

**Table 1.1** A list of pollutant types released from different sources which compose the industrial and municipal waste

| Type of industries | Organic pollutant | References | Inorganic pollutant | References |
|---|---|---|---|---|
| Industrial waste | | | | |
| Pulp and paper industry | Lignocellulosic waste, cellulose, lignin, phenols, tannins, resins, and fatty acid | Singh and Chandra (2019) | Ferrous, magnesium, zinc, copper, nickel | Singh and Chandra (2019) |
| Textile industries | Organic matter | Tüfekci et al. (2007) | Sulphate, sulphide, chloride, calcium, magnesium | Paul et al. (2012), Madhav et al. (2018) |
| Food processing | Organic matter (protein, carbohydrate, lipid) | Parnaudeau et al. (2006), Kroyer (1995) | Nitrogen, phosphorous, potassium | Kroyer (1995), Qasim and Mane (2013) |
| | Organic carbon | Ji et al. (2015) | Calcium, iron, aluminium | Ji et al. (2015) |
| | Pathogen | Manasa and Mehta (2020) | | |
| | Suspended oil, grease | Kroyer (1995) | | |
| Mining | Organic matter | Papirio et al. (2013) | Hydrochloric acid | Cui et al. (2016) |
| | | | Hydrogen sulphide | Kesieme et al. (2012) |
| | Organic carbon | Cravotta III and Brady (2015) | Suspended solids, metals (lead, thallium, nickel, mercury, arsenic, arsenite, cadmium) | Pan (2009), Kumar et al. (2013), Uetani (2007) |

(continued)

**Table 1.1** (continued)

| Type of industries | Organic pollutant | References | Inorganic pollutant | References |
|---|---|---|---|---|
| Petroleum industry and chemical plants | Oil, phenol, Neptha | Allen (2008) | Lead compounds, cyanide, sulphate, mercury, nickel, Zinc | Borah et al. (2020) |
| | Mercaptans, grease | Varjani et al. (2020) | | |
| | Benzene | Jephcote and Mah (2019) | | |
| | Chlorinated dibenzo-*p*-dioxins and dibenzofurans | Dyke and Amendola (2007) | | |
| Pharmaceutical industry | Endocrine-disrupting compounds, steroids, vitamins | Gadipelly et al. (2014) | Cyanide, halides, arsenite, metals, nitrates | Gadipelly et al. (2014) |
| | Acetone | Wang et al. (2019a, b) | | |
| | Hydralazine hydrochloride | Patil et al. (2019) | | |
| | Drugs and antibiotics | Bolong et al. (2009), Bielen et al. (2017) | | |
| Iron and steel industry | Organic matter, oil, benzene, phenol | Doushanov (2015) | Cyanide | Singh and Gupta (2016) |
| | | | Sulphate, ammonia, thiocynate, thiosulphate, fluorides | Doushanov (2015) |
| | | | Sulphides, oxides of copper, chromium, cadmium, mercury | Verma and Dwivedi (2013) |
| Municipal waste | | | | |
| Household discharge (including the pharmaceutical discharge) | Food waste | Koch et al. (2016) | Microplastics | Nguyen et al. (2021) |
| | Oil, fatty acids, grease | Pastore et al. (2015) | | |
| | 1,4-dioxane | Karges et al. (2020) | | |
| | Dissolved salt (organic) | Morrison et al. (2001) | Ammonium and phosphate | Goswami et al. (2021) |
| | Bisphenol A | Dos Santos et al. (2021) | | |
| | Poly-fluoroalkyl substances | Banks and Tatlow (2013) | | |
| | Ibuprofen | Slack et al. (2007) | Lead, Chromium, Mercury, and other inorganic pollutants | Slack et al. (2007) |
| | Acetaminophen, caffeine, cotinine, carbamazepine | Costa et al. (2019) | | |
| | Antibiotics, hormones | Hinkle et al. (2005) | | |

(continued)

Table 1.1 (continued)

| Type of industries | Organic pollutant | References | Inorganic pollutant | References |
|---|---|---|---|---|
| Hospital pollutant | Endocrine-disrupting substance | Sarkar et al. (2022) | Mercury and other inorganic hazardous substances | Rana et al. (2019) |
| | Pathogen | Shahzad et al. (2021) | | |
| | Ibuprofen, diclofenac | Vieira et al. (2021) | | |
| | *N*-nitrosodimethylamine | Sarizadeh et al. (2021) | | |
| Laundry discharge | Detergent | Mohamed et al. (2018) | Microplastic, microfibre | Galvão et al. (2020) |
| | Organic carbon, pathogen | Sidin and Mohamed (2021) | | |

## 1.4 Wastewater Related Issues and Challenges Worldwide

Both developed and developing countries encounter more or less water pollution-related problems. The United States is also a developed country, but wastewater infrastructure in the United States is more complex and expensive. Most of the waste is buried beneath the ground of cities and towns, therefore it is difficult and expensive to inspect (Tafuri and Selvakumar 2002). In the United States, pharmaceutical, organic wastewater contaminants and personal care products related contaminants create a rising concern for human health (Barnes et al. 2008; Spongberg and Witter 2008). Report on pharmaceuticals in wastewater was first published in the United States in 1970 (Daughton and Ternes 1999). Pharmaceutical compounds and human hormones are ubiquitous pollutants identified as endocrine-disrupting chemicals (EDCs) which affect or alter the thyroid functioning and causes cancer in humans, and obesity among youth (Kim et al. 2007; Alsen et al. 2021; Perng et al. 2021). In EU states, sewage waste is an important issue that is required to be handled according to the law (Cieślik et al. 2015). Member of EU discharge a million tonnes of dry mass of sewage sludge every year. Approximately 583,100 tonnes of dry matter of municipal waste Poland alone produced during municipal wastewater treatment (Kujawa et al. 2020). The Netherlands and Volga River of Russia also faces problems concerning different pollutants, including micro-pollutants (Vij et al. 2021; Lisina et al. 2021). In Ireland, Domestic Wastewater Treatment System (DWWTS) is a substantial source of nutrients and enteric pathogens, predominantly in the rural areas (Naughton and Hynds 2014). 1,4-dioxane is the cyclic ether which is identified as a carcinogen by the US-EPA, is widely distributed in the rivers of Germany (Karges et al. 2018). Polycyclic aromatic hydrocarbons (PAHs) are a type of pollutant found both naturally and anthropogenically (Pampanin 2017). Industrial and municipal waste, oil spills, incomplete burning are some reasons for the anthropogenic discharge of PAHs in the Volturno river of Italy (Montuori et al. 2020). Release of the insufficiently treated domestic wastewater pollutants through direct discharge leads to surplus nutrient enrichment that results in eutrophication and algal blooms (Gill et al. 2009; Palmer-Felgate et al. 2010; Withers et al. 2012). The integrated water resource management concept application and attainment of the objectives of the Water Framework Directive (WFD) needs to be solved in a unified way to issues linked to the water use cycle (Teodosiu et al. 2012, 2015; Lemos et al. 2013). The Seine River is one of the most important rivers of France, but due to anthropogenic activities large quantity of metals, chemicals, and pathogens have been accumulated in the river (Le Gall et al. 2018). In developed country wastewater collection and treatment have common practices, and its reuse is practiced with proper attention of environmental protection and health attention (Jimenez and Asano 2008). Poly-fluoroalkyl substances (PFAS) are synthetic and inert compounds that are frequently used since the 1950s in industries and consumer products (Banks and Tatlow 2013). In Australia PFAS are used for firefighting action in Defence Force bases from the 1970s and also used for industrial purposes, that leads to their accumulation in environment which causes many health-related issues (Banwell et al. 2021).

In developing countries, effective wastewater management is not well established in comparison to a developed country. People of these countries lack access to water and sanitation, causing multiple diseases across the population (Libhaber and Orozco-Jaramillo 2012). Water-related diseases affect approximately 2.3 billion people around the globe most of which are the citizens of India and Pakistan (Jalan and Ravallion 2003; Azizullah et al. 2011). In the two-third of rivers of Asia, Africa, and Latin America, the concentration of disease-causing bacteria has increased between 1990 and 2010. In Africa, water-borne diseases infect millions of people (Fenwick 2006). In Latin America, organic pollutants affect about one of every seven kilometres of all river stretch. Due to the lack of effective measures, the eutrophication problem is more severe in Latin American and African countries than in North America and Europe. The global freshwater quality Database (GEMStat) in developing countries is low in density compared to developed countries (UNEP 2016).

Wastewater treatment plants (WWTP) consume more energy for processing waste, associated with higher carbon emissions (Wang et al. 2016). Because of discharging a large amount of wastewater and its productive use in irrigation, it ultimately affects health (Qadir et al. 2010). All over the world, China is the most populated developing country which faces major challenges of accessibility and water quality, including the magnitude and diversity of the country and its rivers (Zhu et al. 2018). Constantly large amounts of pollutants are released into the river and cause eutrophication (Qu and Fan 2010).

Moreover, unplanned urban development has prioritized water services and sewerage, leading to a disparity amid existing water resources and water excellence security, so wastewater treatment and solid waste removal has lagged (Moscoso et al. 2002). Energy consumption in the water sector of Latin America and Caribbean is likely to grow due to the enhancement in the number of treatment facilities required for recovering the present treatment coverage (Noyola et al. 2012). According to United Nations (UN) World Water Development Report (UN WWDR 2021) poor regulation, management, and lack of investment are major obstacles in providing hygienic water to all. Bangladesh, India, Sri Lanka, Nepal are the South Asian countries having water-rich regions, but they show spatial variability, and there has also been great disparity in the strictness of monitoring and enforcement of regulations (Helmer and Hespanhol 1997). Every day, approximately 10.5 million gallons of wastewater are discharged into the water resource (Hirani and Dimble 2019). In India, there are many rivers, but Ganga and Yamuna are the most polluted rivers (Sarker et al. 2021) being the lifeline of indo-Gangetic plain. Thus, there is an immediate concern for the prevention of inadequate and unchecked discharge of industrial and municipal wastewater into the water bodies for pollution prevention.

## 1.5 Health Concerns Due to Water Pollution

WHO defines health as “a state of complete physical, mental and social wellbeing” (Brinkel et al. 2009), and individual health should be sound for proper growth and development. Water is essential and precious, but many people don’t have right to use to clean drinking water, and die due to water-borne bacterial, viral, and fungal infections (Cabral 2010). More than 3 billion people have been at risk and lack adequate access to hand hygiene facilities (UN WWDR 2021). Moreover, women are at risk due to the consistent water use from different water resources such as rivers or lakes for washing cloth and storing water for household purposes (UNEP 2021).

Worldwide, more than 80% of wastewater is neither collected nor treated, and is discharged directly into the environment devoid of appropriate handling (UN WWDR 2020). Few trace elements are essential for the human body (Camur et al. 2021). However, if their concentration exceeds the permissible limit, it affects living organisms (Izah et al. 2016). There are 12 heavy metals which are poisonous when found above the permissible concentration including arsenic, mercury, chromium, nickel, cadmium, cobalt causing disease in humans. These toxic metals are five times denser than water and are not easily removed from the water bodies (Ekpo et al. 2008). Arsenic is ubiquitous and both natural and anthropogenic activity causes its contamination (Ng et al. 2003). Water contamination by natural phenomenon is influenced by hydrological and geological properties of the allied aquatic source (Singh et al. 2021). Consumption of arsenic contaminated drinking water for a longer duration causes toxicity and is detrimental to human (Spallholz et al. 2004; Khan et al. 2007). Furthermore, it shows carcinogenic activity. Arsenicals (a chemical compound that contains arsenic) causes lung, skin, and bladder cancer, but clinical indicators of chronic arsenicosis (accumulation of arsenic in the body due to long-term exposure from drinking water) in people accounts non-cancerous effects like keratosis, hyper or hypopigmentation, cardiovascular ailments, hypertension, and diabetes (Ng et al. 2003; Kapaj et al. 2006; Sun et al. 2016). It is estimated that approximately 60–100 million people in India and Bangladesh face the risk of consuming arsenic-contaminated water (Ahmad 2001; Chakraborti et al. 2001).

Mercury is another toxic metal that causes health-related issues (Budnik and Casteleyn 2019). Mercury exists in various conformation, such as elemental, inorganic and organic mercury compounds. Mercury is released in the environment both naturally and by anthropogenic means. Natural means include volcanic activity, weathering of rocks that contribute to water resources. Anthropogenic sources include mercury and gold mining, cement manufacture, industrial leaks, dentistry, etc. (WHO 2007). The most common disease caused due to mercury is Minamata (methyl mercury poisoning) caused by methyl mercury-contaminated pollutant (Yorifuji et al. 2013; Takaoka et al. 2018). Methyl mercury leads to a form of food poisoning which shows the symptoms like sensitivity disorders, cerebellar ataxia, mental retardation, visual and hearing disorders, deformed or functionally weakened limbs, paralysis, coma, and sometimes even death (Yorifuji et al. 2013). Moreover, the disease-causing methyl mercury is also transported through the placenta to wreak the development of unborn children, which often cause stern mental and physical problems lately in their life (Harada 1978; Harada et al. 2005). Mercury-induced immune toxicity causes risk for infectious diseases, such as malarial infection (Silbergeld et al. 2005).

Fluoride is an essential element for human health in lower amount (Yadav et al. 2019). However, beyond 1.3 mg/l which is a limit set by WHO, it is harmful to human health. In excess dose it causes severe gastroenteritis, restlessness, anorexia, muscle weakness, stiffness, dyspnoea, ventricular abnormalities, and tachycardia (Sahu et al. 2017), bone abnormalities, reproductive organs impairment, muscle and nerve degeneration and particularly the disease fluorosis. Fluorosis can be dental or skeletal fluorosis (Yadav et al. 2019). Due to the uptake of excess fluoride containing drinking water during the tooth development, dental fluorosis or hypoplasia occurs, in which teeth become hard and frangible, leads to mottling, discoloration, and pit formation in enamel (Yadav et al. 2019). Decline in bone mass, joint pain, and hardening of joints are some of the other symptoms of this disease. Asian countries especially India, face fluoride contamination in water resources. It is observed that fluoride concentration is higher in India than in other Asian countries (Yadav et al. 2019). Fluorosis is endemic in at least 25 countries throughout the Asian continent (Fawell et al. 2006). In India, fluorosis is very severe in Andhra Pradesh, Gujarat, and North Rajasthan. Punjab, Haryana, Madhya Pradesh, and Maharashtra are affected slightly, whereas Assam, Bihar, Tamil Nadu, Uttar Pradesh, and West Bengal, are affected the least (Arlappa et al. 2013).

Cadmium is classified as a pollutant in water, that has been reported from all around the world, causing considerable death annually (Fatima et al. 2019). According to WHO guideline, adequate cadmium concentration should be 3 μg/l, while above this concentration, Cd can accumulate in the human body and affect human health (Segawa et al. 2021). Cd causes osteoporosis, renal tubular dysfunction and also causes Itai-Itai disease which leads to severe bone pain (Kasuya et al. 1992). Copper is an essential nutrient, but its higher concentration in drinking water causes anaemia, liver cirrhosis, and kidney damage (Akpor et al. 2014). Likewise, many pharmaceutical pollutants are carcinogenic (Bonefeld-Jorgensen et al. 2011). A compound PFCs (Perfluorinated compound) is a pharmaceutical pollutant which is a severe health hazard causing pre-eclampsia, congenital disabilities, reduced human fertility (Webster 2010), immune-toxicity (Seyoum et al. 2020), and neurotoxicity (Lee and Viberg 2013).

Water-related infectious diseases are classified into four categories: water-borne disease, water-washed disease, water-based disease, and water-related insect disease (Manetu and Karanja 2021). Water resource contamination by water-borne pathogens and the linked diseases are a major problem worldwide (Pandey et al. 2014). Water-borne diseases are threat caused by bacteria, viruses, protozoa and transmitted via ingestion of contaminated drinking water or animal faeces or urine containing pathogens such as cholera, diarrhoeal disease, typhoid, infectious hepatitis, etc. (Woodall 2009; Collier et al. 2021). Various bacterial, viral, and protozoan pathogens excreted in faeces can initiate water-borne infection (Leclerc et al. 2002). Passive carriers of the infectious agent of gastrointestinal illness are different microbes and germs that cause diseases showing symptoms like diarrhoea, nausea, vomiting, fever, and abdominal pain (Arnone and Perdek Walling 2007). *Adenovirus, Cryptosporidium*, *E. coli, Giardia, Shigella spp, Leptospira, Naegleria fowleri, Salmonella, and Vibrio cholera* are the agents responsible for many outbreaks (Craun et al. 2006). In any developing country, majority of people get affected by the diarrhoeal disease due to lack of proper water management and the unhygienic condition and the diseases are easily transmitted from people to people. The people in countries of Asia and Africa are mostly infected by microbial diseases spread through the use or consumption of contaminated water (Seas et al. 2000).

Water-washed diseases are infectious diseases that are transferred by unhygienic lifestyles or lack of water for hand washing and bathing, such as dermatophytosis disease caused by *Trichophyton,* trachoma, Ophthalmia Neonatorum, etc. (Webber 2009; Sobsey 2015). Water-based diseases are infectious diseases that are spread through aquatic host organisms that carry parasitic pathogens such as flat worms schistosomes (Schistosomiasis) and guinea worm Dracunculus (Dracunculiasis). Malaria, yellow fever, dengue fever, filariasis, are an example of water-related diseases caused by an insect that breeds in water (Greenaway 2004; UNICEF 2008) (Fig. 1.2).

## 1.6 Control and Treatment Technologies for Water Pollution

The pollution load and quality control are critical for proper water quality maintenance and for sustainable development of water resources, continuous endeavours are required to lower the water pollution and improve its quality (Singh and Singh 2021). Pollution prevention is an essential and predominant factor that reduces or minimizes the pollutant generated from a point source (Weng et al. 2012). The strategy of pollution control seeks management of pollutants and reduction of their effect on the environment. The best way to control pollution is to prevent it from

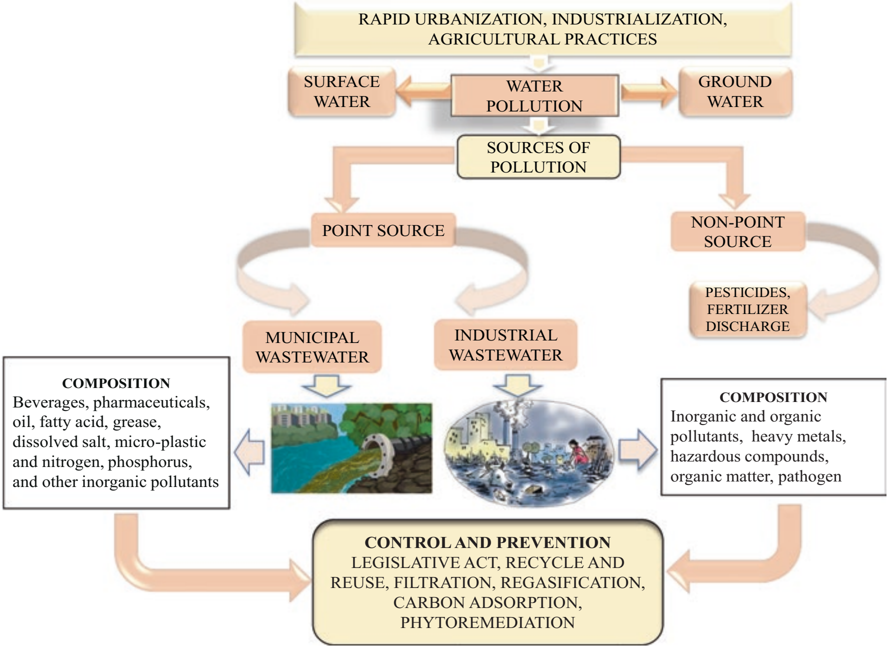

**Fig. 1.2** Sources of water pollution, composition of the municipal and industrial wastewater and control and prevention of water pollution

being created in the first place. This demands the development of new technologies that are environment friendly, efficient, and produce least quantity of pollutants. Furthermore, the sustainable use of natural resources is significant to achieve the goal. Generally, there are two important policies for controlling environmental pollution, which includes the obligatory means and economic incentive. Developed and developing nations both have taken the mandatory means for permitting licenses and implementing the environmental rules (Wang 2006). Legislative acts and regulations are an important tool for controlling water pollution. The instrument of enforcement includes administrative and judiciary means of control. Administrative pressure, warning, amendment, financial damage, fines, and imprisonment are some administrative and judiciary regulations by which we can control the pollution (Warmer and Dokkum 2001). Population control, recycle, and reuse of different industrial products are methods to reduce water pollution (Warmer and Dokkum 2001).

It is important to identify the characteristics of the origin of pollutants. Integrated long short-term memory networks (LSTM) and the Internet of Things are utilized in identifying the characteristics of water pollutants (Wang et al. 2019a, b). Biodegradation, chemical oxidation, enzymatic methods, adsorption, membrane filtration, cementation are some methods used for the removal of industrial effluents (Singh and Singh 2002; Mantzavinos and Psillakis 2004; Noorjahan 2014;

Al-Saydeh et al. 2017; Singh et al. 2018). Common effluent treatment plants (CETPs) are one of the feasible wastewater treatment solutions (Devda et al. 2021). Other methods such as water reclamation, biosorption, and electrochemical technique are also used for this purpose (Volesky 1990; Vo et al. 2014; Devda et al. 2021). For removing heavy metals, and organic and inorganic pollutants from the wastewater system, green and biosynthesized nano-catalyst are used (Eskandarinezhad et al. 2021). Phycoremediation is a cost-effective, environment friendly method used to treat wastewater of food processing industry. Both microalgae and macro-algae are used in the process of phycoremediation (Olguín 2003; Munoz and Guieysse 2006; Gani et al. 2016). Global Freshwater Monitoring Station (GEMStat) should be established all over the country for better analysis of water quality. Awareness about the cause and effects of industrial wastewater should be spread all over the country through NGOs, government, strong institutions, and educated people (Srivastava et al. 2016).

Emerging contaminants threaten the aqueous environment because their persistent occurrence adversely affects all forms of living organisms (Parida et al. 2021). We can reduce the toxicity of municipal wastewater by following different methods. The legislative Act is the most important and regulating method to control pollutant discharge. In India, the water (prevention and control of pollution) Act 1974 was enforced by parliament for solving the problem related to the environment and safety of flora and fauna (CPCB 2021b). Ganga action plan and national river plan address the task of trapping, redirection, and municipal wastewater treatment. Usually, many of the country's wastewater from domestic sources is rarely treated owing to the inadequate sanitation facilities. The use of wastewater in agriculture is an ideal method of irrigation instead of freshwater (Contreras et al. 2017). Domestic and treated water have phosphorous, nitrogen, potassium, and sulphur. These nutrients are accumulated by the plants easily, therefore they are widely used for irrigation (Mara 2009; Drechsel and Evans 2010; Sengupta et al. 2015; Poustie et al. 2020). Nutrient-rich wastewater reduces the use of fertilizers, increases the productivity of crop, can improve the soil fertility, and reduce the cost of production. (Chen et al. 2013; Jeong et al. 2016).

Most of the water pollutants can be removed by both conventional and non-conventional processes. For instance, to avoid nitrate contamination in drinking water and its adverse effect, conventional decontamination technologies are used all over the world (Ahamad et al. 2018). The most common methods are filtration, degasification, sedimentation, adsorption, reverse osmosis, precipitation, and flocculation. Adsorption and membrane separation methods are applied to control the municipal wastewater pollution and are more effective than conventional techniques and well-known recovery processes. These methods have the notable power of removing wastewater pollutants (Saravanan et al. 2021). Pre-coat filtration, slow sand filtration, granular high-rate filtration are some methods that are used to eliminate different microbes such as viruses, bacteria, protozoa, etc. (WHO 2017). Awareness of solid-liquid waste management (SLWM), sustainable use of resources, sustainable urban design are the methods through which municipal pollutants discharge can be reduced. Moreover, treated municipal wastewater can be used as a water source for sustainable aquaculture (Zaibel et al. 2021).

Water-related emerging contaminants are the most challenging issue currently all over the world. For solving this problem various treatment technologies are used frequently. Ultraviolet light-emitting diodes is a modern technique utilized for removing organic pollutants through an advanced oxidation process (Matafonova and Batoev 2018). Electrochemical advanced oxidation process methods eliminate majority of pollutants from wastewater (Monteil et al. 2019). Porous carbonaceous material, i.e., biochar is obtained through the thermochemical decomposition of biomass feedstock used in biochar technologies for wastewater treatment (Xiang et al. 2020). Metal-organic framework (MOFs), peracetic acid-based advanced oxidation processes, three-dimensional graphene-based hybrid material are other methods practiced for the water treatment (Wang et al. 2019a, b; Li et al. 2020; Ao et al. 2021). Ferrates is an iron-based technique used for removing contamination from water which is the tetraoxy iron, eco-friendly, used as a disinfectant for deactivating micro-organisms (Sharma et al. 2015). Membrane bioreactor and hybrid reactor systems are used for removing micropollutants from wastewater. In a Hybrid reactor system, combination of techniques is applied for treatment purposes (Goswami et al. 2018). Besides these technologies, some nanoparticle-based materials such as green-synthesized nanocatalysts, nano adsorbents, and nano metals, are frequently used for eliminating and degrading variant types of hazardous pollutants. Sol-gel based copper–ceria adsorbent is a technique used for removing cadmium from the environment (Pal et al. 2021). Remediation of pharmaceutical hazardous substances, especially antibiotics that affects human health is carried out by biogenic nanomaterials (Nasrollahzadeh et al. 2021; Ojha et al. 2021). The synthetic pollutants such as chlorinated phenolic compounds, inorganic metals, polycyclic aromatic hydrocarbons, absorbable organic halides, phthalates, etc. released in the environment can be degraded by microbial engineering (Schwarzenbach et al. 2006; Kurwadkar 2019; Bhatt et al. 2020, 2021).

## 1.7 Major Action Taken by Various Organizations

According to the United Nations (UN), clean water is necessary for human health, socio-economic advancement, and the ecosystem. However, due to the excess population, nature and its resources are being depleted and degraded. It has been becoming a challenge to ensure a sufficient and safe water supply for each individual. The only remedy for it is to discharge less pollution and improve the wastewater treatment method. On March 22, world water day is celebrated by the UN since 1993. The UN world water report was published on March 21, 2021, as “valuing water.” The 2021 edition of the United Nations World Development Report (UN WWDR 2021) is divided into five interrelated perspectives valuing water source, ecosystem and in situ water resources, valuing water infrastructure, valuing water service, valuing water as an input to production and socio-economic activity. Today we need to improve the current status of water bodies through water resource management for achieving sustainable goal no. 6 i.e., clean water and sanitation of the United Nations 2030 Agenda for sustainable development (UN WWDR 2021).

Global programme for protecting the marine environment from land-based activity focuses on regulating and reducing wastewater, marine litter, and excess nutrients. A program of UNEP is GEMS/water programme (Global Environment Monitoring System for Water) which supports all countries for monitoring and reporting on water quality. In 1978 GEMS/water programme was established, which mainly works to collect global inland water quality data and promote nature-based solutions for water management. Currently, GEMStat (Global Environment Monitoring Station) has data from more than hundred countries (UNEP 2016).

Moreover, World Bank provides financial assistance to the country for improving water quality for both fresh water and the ocean. It focuses on remediation of contamination sites (World Bank 2020). World Wide Fund for Nature (WWF) is the most important and world largest independent conservation organization. This organization works to conserve the planet's natural environment and aim for a future in which humans live in congruence with the nature practicing sustainable use of natural resources. According to the freshwater living planet index, freshwater biodiversity is rapidly declining compared to oceans or forests. Approximately 90% of the global wetlands have been lost, due to anthropogenic activity and have impacted millions of rivers (WWF 2020).

For public health, the World health organization (WHO) released their fourth edition guideline (2017) for drinking water safety. This document consists of all water quality data such as different chemical discharge, microbial contamination (bacteria, virus, fungi, etc.), radioactive pollutant, water-borne diseases, and managing their risk. It also deals with public health according to local and national authorities and water safety plan (Table 1.2).

**Table 1.2** Guideline for chemicals from industrial source and sewage that are of health significance in drinking water (WHO 2017)

| Guideline values for naturally occurring chemicals | mg/L |
|---|---|
| *Inorganic chemicals* | |
| Fluoride | 1.5 |
| Arsenic | 0.01 |
| Barium | 1.3 |
| Chromium | 0.05 |
| Guideline value for chemical released from industries and municipal water | |
| *Inorganic chemicals* | |
| Mercury | 0.006 |
| Cadmium | 0.003 |
| *Organic chemicals* | |
| Benzene | 0.01 |
| Toluene | 0.7 |
| Tetrachloroethene | 0.04 |
| Nitrilotriacetic acid | 0.2 |

The Water (Prevention and Control of Pollution) Act was enacted in 1974 to reduce and prevent water pollution and restore good quality of water in the country. This Act was further revised in 1988 and then in 2003. Cess Act was enacted in 1977 on the person/organization who consumes water for operating different industries. Collected cess is used to increase the State Board's and Central Board's resources to control and prevent the pollution of water constituted under the Water (Prevention and Control of Pollution) Act, 1974 (CPCB 2021b).

The flagship Programme Namami Gange was launched by Union Government in June 2014 costed a budget of Rs. 20,000 crores to achieve protection and rejuvenation of the River Ganga integrated Programme. The Namami Gange Programme has eight pillars, viz. river surface cleaning, river-front development, sewerage treatment infrastructure, afforestation, biodiversity, industrial effluent monitoring, public awareness, and Ganga Gram. In Indian states (Uttar Pradesh, Uttarakhand, Jharkhand, Bihar, and West Bengal), 63 sewerage management schemes are under implementation to create a sewerage capacity of 1187.33 million litres per day (NMCG 2021). Campaigns such as workshops, conferences, events, seminars, and various Information, Education, and Communication (IEC) activities were planned to make public aware of their involvement in the programme. Numerous awareness events/activities were organized through campaigns, rallies, exhibitions, cleanliness and plantation drive, competitions, development, and resource distribution. For widespread publicity, mass media such as television/Radio, media advertisements, featured articles, were published (NMCG 2021). Around 1674 gram panchayat near river Ganga was identified as gram Ganga and funded by the Ministry of Drinking Water and Sanitation (MoDWS) in five states which are Uttar Pradesh, Uttarakhand, Jharkhand, Bihar, and West Bengal for construction of toilet. Out of the targeted 1,527,105 units approximately 853,397 toilets were constructed (NMCG 2021).

Prime Minister of India launched Swachh Bharat Mission with two Sub-Missions, the Swachh Bharat Mission (Gramin) and the Swachh Bharat Mission (Urban), on October 2, 2014 to achieve and accelerate universal sanitation coverage. This mission allows village, panchayat, district, union territories and states, in India to declare themselves "open-defecation free" (ODF) by October 2, 2019, by building over 100 million toilets in rural India. The second segment of the Swachh Bharat Mission (Grameen) has been also launched to drive the facilities to ensure the liquid and solid waste management, i.e., ODF-Plus which will reinforce ODF behaviours and focus on providing interventions for the safe management of liquid and solid waste in the villages (SBMG 2021).

## 1.8 Conclusion

After reviewing the scenario of water pollution, we conclude that there is an urgent requirement for in-depth analysis (i.e., proper monitoring, assessment, collecting data, and strong institution) and planning to protect the earth and achieve UN sustainable goals for our better life in the present and future. Our understanding suggests that the government's policies for regulating the economy, technology, and environment determine the course of water conservation. The current situation demands the treatment of anthropogenic industrial and municipal waste before they are discharged into the water resources. The majority of the developing nations are devoid of advanced wastewater management infrastructure, and therefore, the industries lack the equipment to carry out waste management. Intensive investment in research and innovation will help us discover innovative and efficient strategies to tackle water pollution, ultimately having immense health benefits. Serious efforts are required to make drinking water as safe as possible. Further, modifying national economy policies from extensive to intensive mode causes a reduction in water consumption and paves the way for investment in water-saving technologies and affordable policy. Additionally, to ensure safe drinking water to the public, it is required to carry the regular microbiological analysis of drinking water by assaying the presence of different microbes by culture media. The government should invest financial resources to understand better the ecology and behaviour of human and animal faecal bacteria in environmental waters. Further, subsidies from the government are required for the enhancement of water infrastructure in developing nations. Applying economic strategies for water resource allocation is suitable and offers a simple tool for developing water services more efficiently. Yet, the same should not be followed for water use for domestic needs, specifically for individuals living in extreme poverty. More research, analysis, discussion, and pledges are desirable in deciding whether water is a common or economic good. Understanding the future water quality parameters can pave the way for designing efficient and accurate monitoring programmes for the assessment and prevention of water pollution. Adoption of clever strategies such as using treated tailwater for construction purposes such as road construction. Further, the issue of heavy metal contamination can be tackled by adopting environmental sustainability and various biological treatment processes, mainly microbial and phytoremediation. Additionally, terrestrial vegetation plays a crucial role in the recycling of various toxic inorganic heavy metal waste.

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# Chapter 2
# Adsorptive Remediation of Pollutants from Wastewater

**Zeenat Arif, Naresh K. Sethy, Pradeep Kumar Mishra, and P. Kumar**

**Abstract** An exponential increase in demand of water, commonly known as green and universal solvent is known to have multiple applications in different sectors including domestic, agricultural, and industries. Industrialization, the "pillar of economic development" has greatly affected our water resources since last decade attributed to an increase in the percentage of grossly polluting industries (GPIs) from 1162 to 2743 units. Water being a necessity of livelihood, it becomes necessary to treat it before discharging. This study incorporates the different techniques available to wastewater treatment and primarily focuses on the adsorption remediation as this is an easy/simple and cost-effective technique for wastewater treatment. Emphasis will also be given on the different types of adsorptive material available and the parameters affecting adsorption technique such amount of adsorptive material, time, pH, etc. to improve the water quality and study of different mathematical models to get the better understanding of the technique. Lastly, the chapter will be concluded by highlighting the major research gap and future scope of adopting the present technique and modification needed to improve its performance without compromising much with the production cost.

**Keywords** Adsorption · Industrialization · Quality · Wastewater

## 2.1 Introduction to Water Pollutants

Environmental pollution and energy crisis is increasing and environmental components (air, land, lakes and rivers, oceans, soil, forests, etc.) are getting degraded due to rising population and increasing industrialization. Environmental pollution has

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become threatening issue due to exponential rise in industries and urbanization grew at a fast pace (Onac et al. 2019). Industrial pollutants from different processes releases metal ions or recalcitrant organic molecules, which create long-term adverse effects as they are persistent in water bodies. This resulted in increasing pollution of air and water bodies. According to World Health Organization (WHO) report, presently one-third of the world's population are already facing the challenges of water tension and by 2030 it is projected to increase by 62% (Alejo et al. 2017; Anjum et al. 2018). The major concern lies in the water resources contamination by a variety of pollutants (Gopinath and Kadirvelu 2018).

The presence of heavy metals, nutrient, industrial waste in water are referred as inorganic pollutant (Zhang et al. 2020). Being non-biodegradable, their major source is increased in anthropogenic activities and leads to serious diseases if get accumulated in the human body through drinking water. Organic pollutants, on other hand, includes agricultural and surface water runoff, sewage discharge, pesticides, pharmaceuticals waste, dyes, and industrial discharges causes negative impact on environment owing to their persistence and bio-accumulation. Discharge of organic and inorganic contaminants produces unpleasant odor from wastewater. Increasing water pollution (due to the presence of inorganic, organic, and biological contaminants) and reducing availability of fresh water for human consumption has made it essential to treat and recycle as much as of polluted water as possible (Feng et al. 2018). To circumvent this, it is desirable to give attention to treatment methods and technologies for their remediation.

## 2.2 Treatment Technology

Need for augmenting the available fresh water and recycling of polluted water has attracted global attention towards developing cost-effective, efficient, and sustainable water purification and a wastewater treatment system. Several biological, chemical, and physical processes for treating contaminated and polluted water have been developed and are in use since decades. A brief account of these processes is presented here in the following sections. Broadly, wastewater treatment techniques are classified as conventional, established and emerging methods as shown in Fig. 2.1 to produce clean and safewater. These include adsorption (Warsinger et al. 2018; Singh et al. 2018), electrochemical processes (Jin et al. 2016; Deghles and Kurt 2016), biological operations (Angelucci et al. 2017; Singh et al. 2020), coagulation/flocculation (Mella et al. 2015), chemical precipitation (Borra et al. 2017), solvent extraction (Nayl and Aly 2015), filtration and membrane processes (Bao et al. 2015; Koushkbaghi et al. 2018), electrolysis, ion exchange, reverse osmosis, etc. Selection of a given technique will depend on the wastewater characteristics and level of treatment required. However, out of different technologies available only few are employed by the industrial sector on technological and economic grounds. Table 2.1 enlists the pros and cons of different techniques.

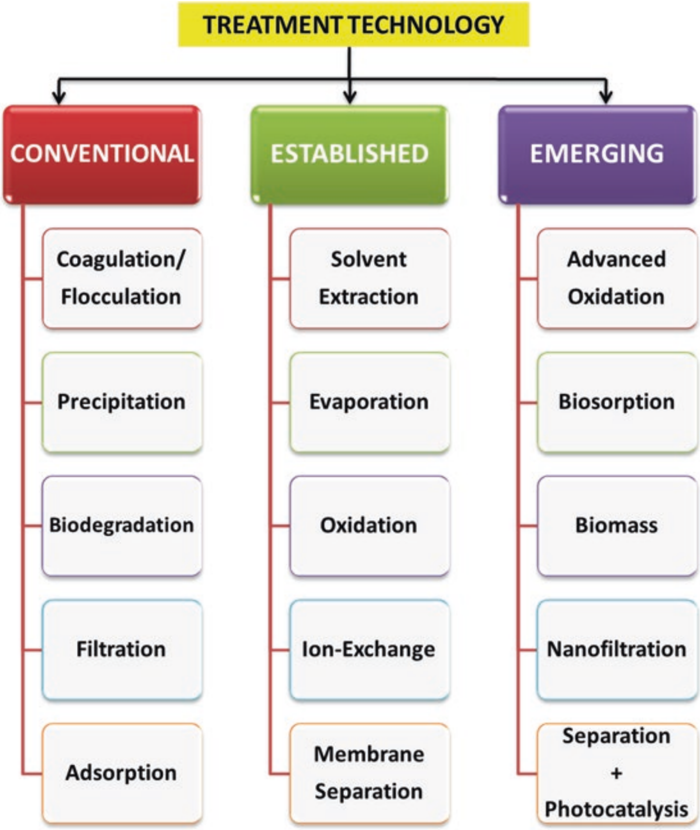

**Fig. 2.1** Classification of technologies available for pollutant removal

## 2.3 Adsorption

Different separation techniques mentioned in the list are linked with drawbacks including capital costs, poor efficiency due to partial removal or involves complex steps for removal of contaminants, sludge generation (unwanted) (Husnain et al. 2020). Adsorption on other hand emerged as a promising water remediation technique owing towards its simplicity, economical from cost point of view, eco-friendly and non-destructive nature, and the availability of a variety of adsorbents (Yaqub et al. 2021). Adsorption is a mass transfer operation in which solute are transported from a bulk phase onto solid surface phase. The deposition/adsorption of solutes involves interactions (electrostatic forces, ion exchange, van der Waals interactions, and chemical binding) between adsorbates and adsorbents which will be responsible for contaminants (organic/inorganic/polar/nonpolar nature) removal (Liu et al. 2020).

**Table 2.1** Pros and cons of different wastewater treatment techniques (Crini and Lichtfouse 2019)

| Process | Pros | Cons |
|---|---|---|
| Chemical precipitation | • Simple technology | • Ineffective metal ion removal capacity |
| | • Economically advantageous | • Increased sludge volume generation |
| | • Adaptability to high pollution load | • High chemical consumption |
| Coagulation/ flocculation | • Simple technology | • Increase in treatment cost due to sludge volume generation which require additional handling and treatment cost |
| | • Low capital cost | • Non-reusable chemical composition is high |
| | • Efficient removal of suspended solids and colloidal particles | |
| | • Improved sludge settling characteristics | |
| | • Significant reduction in the chemical and biological oxygen demand | |
| | • Bacterial growth restricted | |
| Chemical oxidation | • Simple, rapid, and efficient process | • Formation of intermediates |
| | • No sludge production | • No effect on salinity |
| | • Increases biodegradability of product | • Limited effect on chemical oxygen demand |
| Biological methods | • Simple, economically attractive | • Optimal favorable environment for survival of bacteria |
| | • High reduction in biochemical oxygen demand and suspended solids | • Complex microbiological mechanisms and slow process |
| | • Efficient removal of biodegradable organics | • Possible sludge bulking and foaming |
| Adsorption/ filtration | • Simple technology | • Non-destructive and non-selective process |
| | • Quality of treated effluent is high | • Regeneration result in material loss as well as it is costlier also |
| | • Efficient removal of turbidity and suspended solids | • High investment (cost of excellent adsorbent is high) |
| Ion exchange | • Rapid, efficient process and produces treated effluent of a high-quality | • Non-destructive process |
| | • Recovery of valuable metals | • Requirement of large column to treat large volume |
| | | • Fast saturation and clogging of the reactors |
| | | • Initial cost, maintenance, and regeneration costs are high |
| | | • Performance is adversely affected by the effluent pH |

(continued)

**Table 2.1** (continued)

| Process | Pros | Cons |
|---|---|---|
| Electro-coagulation (EC)<br>Electro-flocculation (EF) | • Recovery of valuable metals | • Sludge deposition over the electrodes affect the efficiency as it inhibits the process in continuous operation |
| | • Effective removal of suspended solids, metals, oil, and grease | • Increased cost due to treatment of sludge |
| | • Feasible to treat different pollutant loads of different flow rates | • Maintenance and regeneration is cost is high |
| Membrane separation | • Small space requirement | • Non-destructive separation |
| | • Highly efficient, simple, and rapid process | • Problem of membrane clogging |
| | • Treated effluent is of good quality | • Initial investment, maintenance, and operation cost is high |
| | • Little or no chemicals consumption | • Energy requirement is high |
| | • Generation of solid waste is minimal | |
| Photo-catalytic oxidation | • No consumption of expensive chemicals | • Recovery of photo-catalyst is difficult |
| | • Excellent removal of organic contaminants | • High recombination rate of electron and hole pair |
| | • Successfully applied both in slurry and immobilized reactor | |
| Advanced oxidation process | • No consumption of chemicals | • High pressure and energy intensive process |
| | • No sludge production | • Sensitive to pH of the solution |
| | • Fast degradation | • Low throughput and formation of by-products |
| | • Excellent reduction in chemical and total oxygen demand | |

## 2.4 Types of Adsorptions

On the basis of nature of the surface attachment, adsorption process is classified as physical, chemical, or exchange adsorption (El-sayed 2020)

(a) Physisorption: Physical adsorption caused by Vander Waals forces (weak) without involving sharing or transferring of electron so easy to separate and is essentially reversible.

(b) Chemisorption: Chemical adsorption involves chemical bonding between desired material and adsorbent which are difficult to remove. It is principally irreversible.

(c) Exchange adsorption: Attraction between adsorbate and the charges present on the adsorbent surface is defined as exchange adsorption

## 2.5 Different Types of Adsorbents and Their Properties

Activated carbon, natural minerals Zeolites, alumina, amberlite, biosorbents, metal oxides are few of the different adsorbents that are commercially available for contaminants removal from wastewater (Husnain et al. 2020; Yaqub et al. 2021). Poor selectivity, sluggish adsorption kinetics, and poor adsorption capacities hinders their wide-scale application. Research is being carried out in this area to develop efficient adsorbents that is economical and possess good selectivity. In this pathway, outstanding physicochemical properties, high aspect ratio, reduction/oxidation ability, modified surface chemistry, large surface area with chemical reactivity nanomaterials, two dimensional (2D) materials are center of attraction in this regard (Salim et al. 2019). Details of widely used adsorbents are discussed below.

### *2.5.1 Nanocellulose-Based Composite Materials*

Innovation in advanced nanotechnology leads to production of low-cost product using renewable and sustainable lignocellulose resources. These emerging materials have a tendency to substitute fossil-based materials for removing unwanted substances from wastewater as they are known to possess high adsorption performance (Yuan et al. 2020). Nanocellulose and its composite such as cellulose nanocrystals, nanofibrils, microfibers, nanofibers, and combinations are different types of nanocellulose-based composite materials. These materials have found application in removal of heavy metal ion, oil water separation, dye adsorption, etc. These materials can also be used as membrane, as a catalyst to remove unwanted material from wastewater.

### *2.5.2 Carbon-Based Nanomaterials*

In the application of wastewater treatment, numerous studies were carried out using carbon-based nanomaterials because of their unique properties of having small size with high ratio of surface area to volume thereby possess high reactivity, highly thermal and chemical stable material, and abundance availability at the nanoscale. Different allotropic forms are graphite and its composite, diamond, fullerenes, carbon nanotubes, etc. Multi-walled carbon nanotubes (MWCNTs) can effectively remove Arsenio (III), and methyl orange and red (organic pollutant) from wastewater. Graphene oxide having strong electrostatic repulsion for anionic organic compounds hence proves to be highly efficient material for removing cationic organic pollutants (Madima et al. 2020). Heavy metals released from different industrial sector tannery, electroplating, metal processing industries, fertilizer, pesticide are non-degradable pose serious health threats to living organism at low concentrations.

Graphene and carbon nanotubes-based nanomaterials are used widely in the elimination if toxic metal because of the presence of oxygen-containing functional groups, tunable surface chemistry, non-corrosive property etc.

### *2.5.3 Clay Minerals*

Clay minerals being the most affordable, abundant, naturally occurring. environmentally friendly minerals have a potential to remove many contaminants (Otunola and Ololade 2020). More investigations still needed to carry out the modification. Also, several methods are existing to tailor the properties for the modification in clay minerals to increase adsorption capacity of clay material when used for removal for heavy metals.

### *2.5.4 Metal-Organic Frameworks*

Metal-organic frameworks (MOFs) because of their unique physicochemical property such as large porosity high specific surface area, simple pore structure designing is in great demand. Compared to conventional adsorption materials MOFs showed a better performance. Nowadays functionalized MOFs open a pathway to enhance the removal efficiencies of a contaminant through pre- and post-synthetic modification. Integrating MOFs with other techniques create another option to remove water pollution and such coupling technologies enhances the performance of an individual material (Bian et al. 2018).

### *2.5.5 Graphene*

Graphene and its composite is a 2D structure having single-atom graphite layer; has attracted many application areas such as removal of hazardous contaminants: heavy and rare-earth metal ions, and organic compounds (Ali et al. 2019)

### *2.5.6 Low-Costs Adsorbents*

Cheap and easily available resources include biosorbent, industrial, agricultural solid wastes such as almond shell, cashew nut shell, cotton and gingelly seed, grapefruit peel hazelnut shell, white rice husk ash, wood derived biochar, etc. as shown in Fig. 2.2. Hemicelluloses, lignin, lipids, and hydrocarbons are basic components of agricultural waste with a high potential sorption capacity towards different

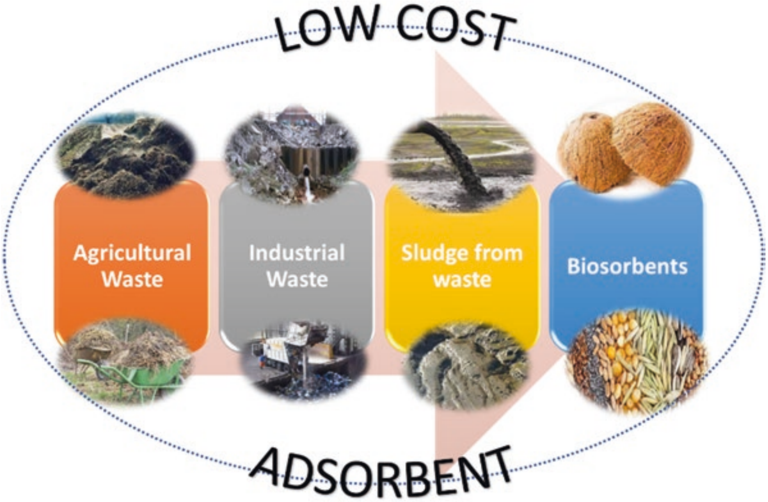

**Fig. 2.2** Different types of low-cost adsorbent

pollutants. For production of granular activated carbon (adsorption capacity >85%) almond, hazelnut shell, etc. are widely used as raw material. Agave bagasse, a by-product of distillery unit, if used as adsorbent has the potential to remove heavy metal ion and can be 45% regenerated after application. Sky fruit husk was used to prepare activated carbon that has surface area of 1211.57 $m^2/g$ and is used to reduce/eliminate anionic herbicide bentazon with adsorption capacity of 166.67 mg/g. Industrial waste also finds its suitable application in the production of adsorbents. For example, steel industry furnace slag, aluminum industry waste as red mad are used as adsorbent to remove organic pollutant from wastewater. Carbonaceous adsorbent from carbon slurry of fertilizer plants is another low-cost adsorbent which can be effectively used to treat different types of pollutant (De Gisi et al. 2016).

## 2.6 Properties of Adsorbents Effecting Adsorption

*Hydrophilicity or hydrophobicity:* Adsorbent hydrophilicity or hydrophobicity is a significant characteristic during separation of molecules from mixtures. Increase in water uptake will be enhanced in the presence of hydrophilic adsorbent in enzymatic treatment. Synthetic and natural zeolites comes under category of hydrophilic adsorbent, whereas bio-based adsorbents exhibit both hydrophilicity and hydrophobicity.

*Adsorbent's particle size:* Impact of adsorbent size on solute concentration is very much high. Larger particle size because of lower specific surface area will reduce final uptake. An increase in the adsorbent surface area increases the number new active sites hence permitting more binding of solute molecules thereby increasing the performance (Karimi et al. 2019).

*Adsorbents pore size:* Adsorbent pore size and molecular diameter plays a significant role in the separation process. Study of Zhang et al. 2018 concludes that larger pore diameter had higher adsorption efficiency. Similar results were also withdrawn by Kumar et al. (2019) for adsorbate pore size >10 nm enhances the adsorption kinetics for phosphate removal.

*Adsorption temperature:* Adsorption process is an exothermic process, so in generalized form it can be said that temperature reduction leads to better separation by adsorption technique.

*Adsorption flow rate:* Flow rate along with retention time plays a crucial role in adsorption in a dynamic process. Darunte et al. 2018 had emphasized that adsorbent mass and flow rate are important parameter in affecting the adsorption capacity for fabricated $NaMn_xO_y$ adsorbent from air calcination and it was found 40–70 times greater than the precursor MOF.

*Feed Concentration:* Increased feed concentration decreases the mass transfer coefficient with increase in mass transfer resistance thereby adsorption efficiency also declines.

## 2.7 Pollutants Remediation by Adsorbent

**Dyes:** The continuous increase in the concentration of toxic dye in the wastewater released from different sectors of industries is a factor of prime concern. Different dyes that are widely used include Congo red (CR), crystal violet, Disperse Violet 26, methylene blue (MB), methyl orange (MO), methyl red, and rhodamine B (RhB) and their main releasing source are industries of different sectors such as cosmetic, food leather, textile, pharmaceutical, also dyes released from household, wastewater treatment plant and their schematic representation is shown in Fig. 2.3.

As per the researches carried out it was estimated that worldwide, production of dye annually is about 70 lakh tons of dyes are produced annually (Dutta et al. 2021). The direct disposal of untreated dye creates mutagenic or teratogenic effects on aquatic organisms. Dutta et al. 2021 also highlighted that comparing the existing advanced oxidation technique, filtration, and biological treatment processes with the adsorption, latter proves to be efficient for treating dye wastewater as it is economical, simple technique, and good recycling of the adsorbents. The adsorption performance of different adsorbents for the treatment of dye-contaminated water is presented in Table 2.2.

**Heavy Metal:** Metals and metalloids (atomic density >4 ± 1 g/cm$^3$) also referred as group of trace elements comes under the category of heavy metal. They are considered as biologically dangerous and the toxic contaminants present in soil and water. Natural and anthropogenic are elemental sources of heavy metals. Possessing high stability, solubility, and migration activity they are dangerous for health and

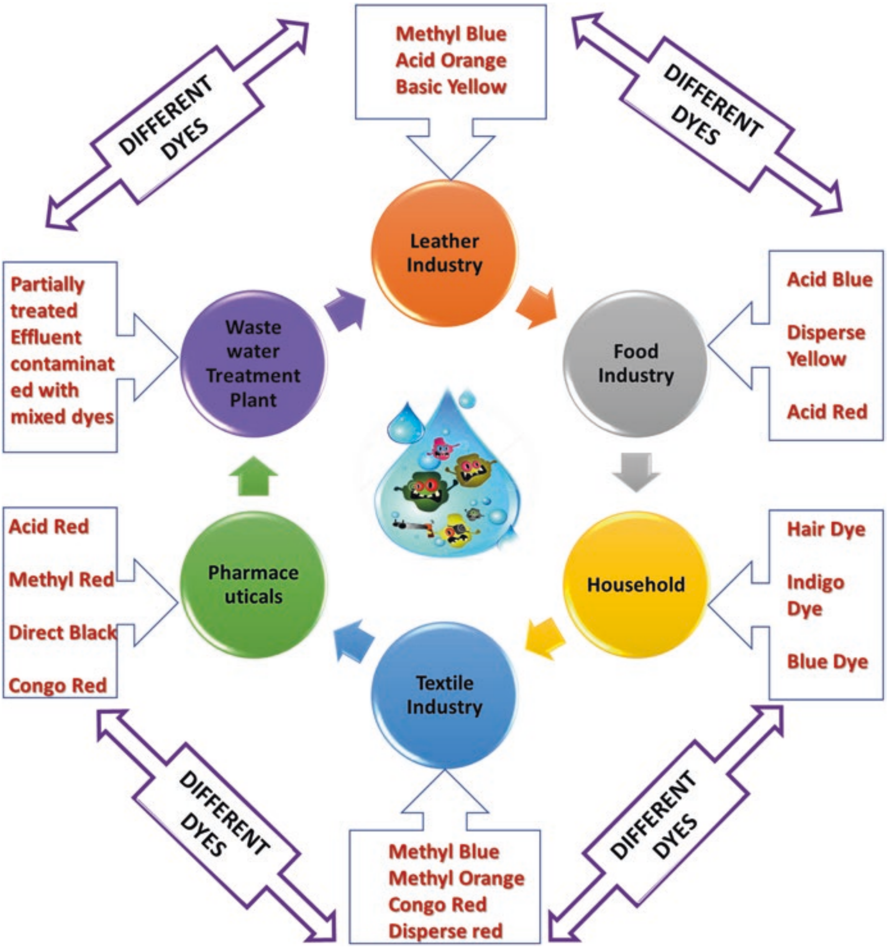

**Fig. 2.3** Source of different types of dyes

environmental when discharged into water above permissible limit. Thus, it necessitates to treat heavy metal contamination to avoid negative consequences on environment (Burakov et al. 2018). Adsorption technique is considered widely for eliminating noxious heavy metal from water because of flexibility in the process design and operation and produces high-quality treated effluents relatively at low cost also their regeneration through desorption is effective as process is reversible.

Adsorbents performance for removal of heavy metal-contaminated water is presented in Table 2.3.

**Surfactants:** Surfactants are persistent, highly soluble, and emerging contaminants (ECs) existing in the water environment. Being soluble they can easily surpass the treatment processes and can reach drinking water resources thereby imposing a

**Table 2.2** Performance of different adsorbents for the treatment of dye

| Adsorbent | Dye | Adsorption capacity | References |
|---|---|---|---|
| Activated carbon and it composite | Congo red (CR) and Direct blue 6 (DB) | 555.56 and 625.00 mg/g<br>Removal efficiency for CR was 62.52% and 50.47% for DB after four cycles was obtained | Patra et al. (2020) |
| | Methylene blue (MB) | 219.9 mg/g at pH 8<br>Adsorption percentage >75% was observed after four cycles | Naushad et al. (2019a) |
| | Malachite green dye (MG) | 66.87 mg/g at pH 7, dye concentration 30 mg | Naushad et al. (2019b) |
| | Congo red | 39.70 at concentration 10 mg/L | Ojedokun and Bello (2017) |
| Nanocomposite of carbon and ultrafine Ni/C | RhB and MB | 5.269 and 7.415 mg/g at concentration 5 mg/L | Kim et al. (2018) |
| Fe–C hybrid magnetic nanosheets157 | CR & MB | 531.9 and 185.2 mg/g | Manippady et al. (2020) |
| Nickel nanoparticles/carbon nanotube | MG, CR, Rh B. MB, MO | Adsorption capacity obtained was 898, 818, 395, 312, and 271 mg/g for MG, CR, RB, MB, and MO, respectively | Jin et al. (2018) |
| $Fe_3O_4$/GO | MB and MO | 666.7 and 714.3 mg/g at dye concentration 1 mg/L | Khajeh and Barkhordar (2020) |
| Zirconium-based MOFs | CV and RhB | 63.38 and 67.73 mg/g at dye concentration 10 mg/L | Ahmad et al. (2020) |
| Pure polyaniline and polypyrrole | CR | 250.01 and 66.66 mg/g at concentration 20 mg/L | Chafai et al. (2017) |

serious health risk to flora and fauna. They are amphipathic molecules with high molecular weight and possess both hydrophilic and hydrophobic components (Siyal et al. 2019. Domestic discharge contains surfactants where concentration lies in the range of 1–10 mg/L whereas surfactant from manufacturing industries concentration reaches to up to 300 mg/L. Sewage treatment plants reduce surfactants concentration to acceptable range but appreciable amount still exist in the sludge which creates environment problem (Siyal et al. 2020). They are also responsible for eutrophication to take place in lakes and treatment plants thus creates unpleasant taste and odor also an increase in the alkyl chain length proportionally increases the surfactants toxicity. Adsorption techniques was found effective in removal of surfactants from wastewater. A large number of adsorbents exist which are used effectively to reduce/eliminate surfactants concentration from discharged water from household/industries and few of them are listed in Table 2.4.

**Emerging Pollutant:** *Pollutants* other than heavy metals, dyes, there exist highly stable structured pollutants whose impact are not known on wastewater, such pollutants are termed as emerging pollutants. Cosmetics, herbicides, pesticides,

**Table 2.3** Adsorbents performance for removal of heavy metal-contaminated water

| Heavy metal | Adsorbent | Maximum adsorption capacity (mg/g) | References |
|---|---|---|---|
| Hexavalent chromium | Microalgal biochar | Adsorption capacity 25.38 at 22 °C<br>Maximum removal efficiency of 100% was achieved | Daneshvar et al. (2019) |
| | Polyaniline@magnetic chitosan | 186.6 mg/g ad adsorption efficiency was >95% after five cycle was observed | Lei et al. (2020) |
| | Polyethyleneimine cross-linked graphene oxide | 436.20 mg/g | Geng et al. (2019) |
| | GO | 43.72 at pH 3 | Yang et al. (2014) |
| | Activated carbon (AC) | 89.5 mg/g at pH 4.5, adsorbent dosage 2.5 g/L | Zhao et al. (2020) |
| $Cu^{2+}$, $Pb^{2+}$, $Cd^{2+}$ | Sulfhydryl modified chitosan | 273.7 mg/g ($Cu^{2+}$), 163.3 mg/g ($Pb^{2+}$), and 183.1 mg/g ($Cd^{2+}$), respectively | Yang et al. (2021) |
| $Hg^{2+}$ | Biochar from corn straw | 75.56 mg/g | Guo et al. (2020) |
| $Cu^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Cd^{2+}$, $Fe^{2+}$ and $Zn^{2+}$ | Modified zeolite | Maximum capacity 91.34 ($Pb^{2+}$), 85.71 ($Cu^{2+}$), 78.27 ($Cd^{2+}$), 76.18 ($Ni^{2+}$), 67.41 ($Zn^{2+}$) and 63.45 ($Fe^{2+}$) mg/g | Mirbaloochzehi et al. (2020) |
| $Ni^{2+}$ | alk-MXene/LDH | 222.7171 mg/g pH > 5 and exhibit removal efficiency of 97.35% | Feng et al. (2020) |
| $Pb^{2+}$ | Modified graphene hydrogel<br>Lignosulfonate with oxygen-containing groups | 1308 | Li et al. (2016) |

pharmaceutical compounds are common example of emerging pollutants. Removal of these pollutants by conventional treatment (primary and secondary processes) are not very effective (Pai et al. 2020). To prevent chronic effects of these pollutants, adsorption is an effective technique for remediation of these pollutants at low concentrations in the wastewater. Pharmaceutical products, such as loxacin and triclosan, were effectively adsorbed by the green route synthesized hydroxyapatite (HAP), synthesized via coprecipitation. The evaluated adsorption capacity of triclosan and loxac were 133.3 and 29.15 mg/g, respectively. In the treatment of herbicide, atrazine, absorption capacity was >95% for atrazine. A removal percentage >95% was achieved at the optimum adsorbent dosage of 10 mg/L and neutral pH (Chaudhary et al. 2018). Composite of biochar not only removes antibiotics but also effectively eliminates heavy metal from aqueous solutions (Li et al. 2020). Biochar doped with nano HAP was used as adsorbent to adsorb copper and tylosin/sulfamethoxazole. Adsorption is due to the existence of hydrogen bonding, π–π

**Table 2.4** Adsorption performance of different adsorbents for surfactants removal

| Surfactants | Adsorbent | Adsorption capacity (mg/g) | References |
|---|---|---|---|
| Sodium dodecyl benzene sulfonate (SDBS) | Cross-linked films of Chitosan | 30.7 | Kahya et al. (2017) |
| | Chitosan | 6.38 | Parhizgar et al. (2017) |
| | Activated carbon derived from pine trees | 97.56 | Valizadeh et al. (2016) |
| | Fly ash based geopolymer (FAGP) | 714.3 | Siyal et al. (2019) |
| | Carbide-derived carbon | 442.4 | Almanassra et al. (2021) |
| Sodium dodecyl sulfate (SDS) | Coal fly ash | 2.95 | Zanoletti et al. (2017) |
| Perfluorosurfactant (PFOS) | Activated carbon | 1320.6 | Schuricht et al. (2017) |
| *t*-octylphenoxy poly ethoxy ethanol (TX-100) | Graphene oxide | 1203 | Prediger et al. (2018) |
| CTAB | Natural zeolite (clinoptilolite) | 113 | Harutyunyan and Pirumyan (2015) |

interactions and adsorption capacity of 160 and 140 mg/g for tylosin and sulfamethoxazole, respectively, was obtained. Diclofenac and fluoxetine were degraded using titania doped HAP.

## 2.8 Adsorption Kinetics Models

Isotherm models that relate equilibrium relationship adsorbate (amount adsorbed) and the remained adsorbate. Isotherm model plays a key role in the system designing and modeling validates the adsorption process. Considering the assumptions associated with each model, the physicochemical parameters could determine adsorbent surface properties, adsorption mechanism, degree of adsorption sites, and affinity between adsorbate and adsorbent (Karimi et al. 2019). The adsorption kinetic evaluate the adsorption rate, performance, and the mass transfer mechanisms which will be used for designing the adsorption systems. The adsorption kinetic involves basic three steps include external diffusion (transfer of adsorbate through the liquid film) followed by internal diffusion (adsorbate diffusion in the pores), lastly adsorbate adsorption on the active sites. As already stated that adsorbate and adsorbent characteristics control the rate of mentioned steps. Adsorption isotherms are used to find the maximum adsorption capacity. Plot between adsorbed molecules per unit area and gas pressure/liquid solution's concentration are referred as adsorption isotherms and are widely accepted method to estimates adsorption

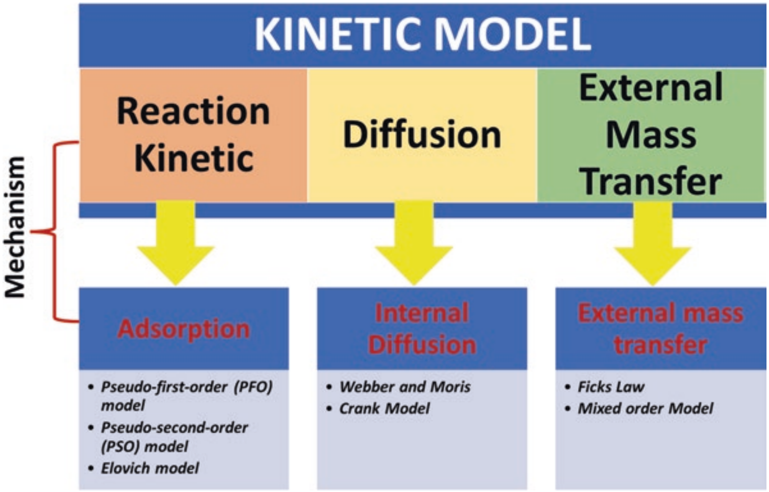

**Fig. 2.4** Kinetic Models and their mechanism

capacity. Langmuir and Freundlich's isotherms are well known models to assess adsorption capacity of material for pollutant adsorption (Wong et al. 2020).

Other than isotherm models, kinetic models include pseudo-first-order (PFO), pseudo-second-order (PSO) model, mixed-order (MO) model, the Ritchie's equation, Elovich model, and the phenomenological mass transfer models are different adsorption kinetics to explain kinetic process (Wang and Guo 2020). Schematic representation of different kinetic model is shown in Fig. 2.4.

However, there are few problems related to these empirical models which includes lack of physical meanings (in case of PFO & PSO), mass transfer mechanisms are difficult to investigate. Also, these models involve use of complicated differential equation which hinders their successful application. Therefore, different models are used under different conditions. Brief study of model and their empirical correlation are explained below.

## *2.8.1 Pseudo-First-Order (PFO) Model*

Proposed by Lagergren (1898)
Differential form in Mathematical representation: $\frac{\mathrm{d}q}{\mathrm{d}t} = k_1 \left( q_e - q_t \right)$
Linearized form: $\ln(q_e - q_t) = \ln q_e - k_1 t$
$q_e$ = equilibrium adsorption, $k_1$—rate constant

### 2.8.2 Pseudo-Second-Order (PSO) Model

Differential form in Mathematical representation: $\frac{\mathrm{d}q}{\mathrm{d}t} = k_2\left(q_\mathrm{e} - q_\mathrm{t}\right)^2$

Linearized form: $\frac{t}{q_\mathrm{t}} = \frac{1}{q_\mathrm{e}^2 k_2} + \frac{1}{q_\mathrm{e}}$

$k_2$—second order rate constant

### 2.8.3 Mixed-Order (MO) Model

Form of mixed-order model is given below

Differential form in Mathematical representation: $\frac{\mathrm{d}q}{\mathrm{d}t} = k_1\left(q_\mathrm{e} - q_\mathrm{t}\right) + k_2\left(q_\mathrm{e} - q_\mathrm{t}\right)$

**Model Assumption**

1. Adsorption at arbitrary stage,
2. Diffusion/adsorption is the rate controlling step, and
3. Arbitrary initial concentration of adsorbate in the solution.

### 2.8.4 Elovich Model

Assumptions of this model are (1) direct relation between activation energy and adsorption time and (2) the adsorbent surface was heterogeneous. The Elovich model is used in the chemisorption of gas onto solid. This model is applied successfully to define metal ion and organic pollutant adsorption on adsorbate

Differential form in Mathematical representation: $\frac{\mathrm{d}q_\mathrm{t}}{\mathrm{d}t} = ae^{-bq_\mathrm{t}}$

Linearized form: $q_\mathrm{t} = \frac{1}{b}\ln\left(abt\right)$

### 2.8.5 Ritchie's Equation

The model is proposed initially to determine kinetics of gases on solids. Physical significance of this equation is it considers only adsorption on active site and does not consider desorption process.

Differential form in Mathematical representation: $\frac{\mathrm{d}\theta}{\mathrm{d}t} = \alpha\left(1-\theta\right)^n$

$\theta$ = ratio of $q_\mathrm{t}$ and $q_\infty$, $n$ = reaction order.

## 2.9 Future Aspects

Developed adsorbents such as carbon, biomaterials, nanoparticles, CNTs have been used to remove toxic impurities from wastewater. Still research is needed in this area to develop a novel adsorbent to build a cost-effective technology for remediation of pollutant from wastewater treatment since the process has certain limitations in terms of enhanced efficiency and activity along with long-term stability. In this context integrating agro-industrial waste and naturally occurring materials or composite made up of industrial waste materials and biodegradable nanomaterials could be research area without compromising with the efficiency at the same time friendly for human health and environmental sustainability. Different aspects still need to consider while modifying adsorbent to enhance its properties. Future trends in research into the adsorption techniques may include:

- Innovation and research in the investigation of adsorbents with minimal environmental footprints.
- Utilization of waste/by-product: Utilization and development of by-product-based adsorbents to improve its economic viability.
- Large scale applications: Development of hybrid and composite adsorbents for surfactant removal.
- Adsorbents Feasibility in treatment of multiple pollutants: Test for adsorbent on wastewaters contaminated with different toxic pollutants to investigate the bonding affinity between adsorbates and adsorbents.
- Selection of nano-adsorbent: Production cost needs to be considered before selection of any nano-adsorbents for their commercial purpose and its separation/reuse ability after application because it may again increase the process cost.
- Disposal: Economical and safe disposal is of prime concern after the application or reuse of exhausted adsorbents.
- Use of spent adsorbents: Spent adsorbents can be used for energy production purposes in fuel cell and to produce biochar.
- Development of adsorbents in pellet/granules form and testing it performance in dynamic adsorption processes in adsorption columns.

## 2.10 Conclusion

The discharge of pollutant in the water bodies has not only depleted the quality of freshwater resources but also results in allergic, carcinogenic, mutagenic effects on living organisms. Different existing treatment techniques with their pros and cons are mentioned, out of which adsorption was considered as a potential technique owing to simplicity, easy application, cost-effective and scalable synthesis of adsorbents, good removal efficiency. In this regard various adsorbents investigated and property was highlighted in respect to adsorption ability. Also, this chapter emphasis on different types of pollutants, their contributing sources, toxic effect, and different types of adsorbents used along with adsorption capacity to eliminate these toxic pollutants. MOFs, metal oxides, active carbon, zeolites, and bio-adsorbents are widely used adsorbents and show good adsorption ability against different contaminants. In recent times low-cost adsorbents, nano adsorbents are perceiving more attention for wastewater owing to their modified textural properties, enhanced porosity with high specific surface in order to increase the adsorption efficiency. The chapter also includes different crucial parameters such as adsorbent dosage, initial feed concentration, temperature, and equilibrium time, affecting the adsorption process and different adsorption kinetic, their mathematical expression are discussed in details. Still there is need to carry out research in this field to treat a wide range of pollutant on large scale as the adsorption technique proves highly efficient at lab scale

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# Chapter 3
# Technological Outline of Constructed Wetlands: An Alternative for Sustainable and Decentralized Wastewater Treatment

**Prashant and Shubham Kumar**

**Abstract** As the population grows, water consumption increases and a large amount of wastewater is generated. The release of untreated wastewater into the aquatic systems is the reason for dilapidated conditions of the water bodies. Intercepting and treating wastewater before it meets the water bodies shall be prioritized in order to protect them, not even in urban but also in rural locations. Constructed wetlands (CW) are emerging and gaining popularity in recent times as a technological option for wastewater treatment. CWs are progressively being applied across the countries for treating variety of wastewaters and it is being looked as an alternative to the conventional wastewater treatment plants. The locally available components and simple design make it decentralized and sustainable choice for wastewater treatment. CWs are based on the principles of ecological engineering; they mimic the natural wetlands processes. The assemblage of soil, substrate, vegetation, microorganisms work cohesively in an engineered system to give desired output of wastewater cleansing.

Varied experimental material and designs have been tested for treating sewage, but the common group of components are water, filter media, vegetation, microorganisms, and liners. The major classes of CW are horizontal and vertical flow CWs. The choice of vertical or horizontal type of treatment units depends on the type of wastewater, desired quality of treatment, and availability of land. The degree of treatment depends on the vegetation material, size of the system, retention period, organic loads, and surface loading. This chapter is a compilation on the design aspects of CWs, their operations details, site selection criteria, treatment mechanisms, and advantages and drawbacks.

**Keywords** Constructed wetlands · sustainable · decentralized · design · operation

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## 3.1 Introduction

Water is the most essential component of the environment any form of life is not possible without water. It is undoubtedly a great solvent and carries variety of chemicals with it in dissolved and suspended forms. Therefore, the water gets polluted easily contaminated. It governs almost all our activities be it domestic need or developmental activities. Metabolic processes of the living organisms are governed by the water, as most of the biochemical mediated reactions within bodies of organisms takes place in aqueous medium. Water has a unique property to dissolve materials in it without altering the chemical properties, so it is excellent in transporting the materials in the body. Water shortage is probably going to turn out to be trickier soon because of fast populace development, expanding per capita water utilization and topographical differences between focuses of populace development and accessibility of water. The increasing population concentrating in urban locations is causing increased generation of wastewater. Lakes, waterways, reservoirs of the world are currently getting contaminated by disposal of wastewater into them and thereby presenting danger to the existence of life forms in water bodies. Wastewater treatment is an issue that has tormented man since the time it was revealed that releasing the waste into inland waters could prompt numerous environmental challenges. The treatment of the wastewater before its disposal into the inland water bodies is one of the solutions to protect water bodies. The choice of a wastewater treatment method is crucial, it depends on various factors like availability of space/land, type of wastewater, degree of treatment required, centralized or decentralized system, energy, and chemical requirements. The conventional wastewater treatment systems involve combination of physical, chemical, and biological treatment processes such as screening, sedimentation, chemical coagulation, filtration, and microbiological activities for the degradation of organics present into the wastewater. The conventional wastewater treatment processes are highly mechanized, concrete, and iron structure that consumes electrical energy to run them. Therefore, it is called energy consuming process of wastewater treatment. In the last 50 years, significant interest has been communicated in the possible utilization of ecological systems to assist wastewater treatment in a controlled way. The natural methods for wastewater treatment like aerobic/anaerobic ponds, constructed wetlands (CWs) and waste stabilization ponds differentiate themselves with the conventional systems as they are combination of natural components like light, gravity, plants and microorganisms working in co-action for treatment of wastewaters. Under these natural systems the natural forces are utilized in managed environment to perform the task, rather using heavy pumps to lift water and motors to run machines.

In the recent decades, constructed wetlands have been tested at laboratory, mesocosm and at field levels. Its diverse applications and treatment efficiency into wastewater treatment, with additional environmental benefits has presented it as promising eco-technology in front of decision makers, scientists, engineers and wastewater treatment solution providing companies. This chapter is presenting the technological outline for its design, operation, treatment mechanisms, environmental advantages, drawbacks and need for future research.

## 3.2 Background

The natural wetlands are unique reservoir of large volume of water, that release the water slowly into the environment. It plays a significant role in climate regulation, ground water recharge, water purification, habitat for variety of biodiversity (wetlands regulating services). The community living close to the wetlands, depends on it for food, fibre, biomass, medicinal plants and freshwaters (wetlands provisioning services). The close association with wetlands is for its ethical purposes, recreation and ecotourism (Cultural values). The wetlands also support for cycling of the nutrients, soil formation and production biomass and gaseous exchange through photosynthesis (Supporting services).

The wetlands are the natural bioreactors as many bio-mediated transformations take place in these systems, like bacteria degrade the organic matter into simpler forms available to the consumers. The combined physical, chemical and biological actions help in water purification process in natural wetlands. The physical process involves sedimentation, chemical processes are chelation, adsorption and precipitation, etc. Prevalent biological processes are nitrification, de-nitrification and ammonification in the presence of variety of microorganism with or without oxygen. The potential of natural wetlands has been recognized by many workers for the purification of water/wastewater (Verhoeven and Meuleman 1999; Gopal 1999). The unique characters of the wetlands system like large amount of water (causing dilution), oxic and anoxic soil substrate responsible for nitrification/de-nitrification and deep rooted emergent macrophytes responsible for biomass accumulation through nutrient uptake, make them to be considered for wastewater disposal and treatment (Nichols 1983). At the same time addition of excess nutrients to the wetlands through agricultural runoff, municipal and industrial sewage cause eutrophication of wetlands (Liu and Diamond 2005).

CWs are the artificial wetlands, ecologically engineered incorporating water, tankage, substrate, flow distributors and macrophytes. CWs may be developed for several reasons part from the most common one, i.e., wastewater treatment. Some legitimate applications of CWs are

- *Constructed wetlands habitat*: these are developed with a reason to provide habitat to the wildlife. Major habitat wetlands are the freshwater swamps and marshes, salt marshes, saltwater swamps, freshwater marshes and swamps.
- *Flood control CWs*: flood control wetlands are developed in a large area with native vegetation. These areas are used for the impoundment of runoff and further slow release of the collected waters.
- *Constructed aquaculture wetlands*: these are mostly used for growing food like fish, prawn chestnut, fox nut, etc.

## 3.3 Constructed Treatment Wetlands

Despite engineered wetlands have been created for fulfilment of multiple functions around the globe. Their wastewater treatment abilities presented them as an alternative option for treatment of range of wastewaters (municipals, landfill, industrial, mining and agricultural) before the researchers. While these systems are space intensive, they provide an effective means of integrating wastewater treatment and resource optimization. Often at costs that are competitive with traditional wastewater treatments. This chapter provides brief descriptions on deign, operation, maintenance and advantages of constructed treatment wetland systems for wastewater treatment.

## 3.4 Development of Constructed Wetlands: Historical Approach

Though Constructed Wetlands technology is new to India, but it has been successfully practiced in many countries like Australia, Denmark, Germany, Japan, U.K., USA, Switzerland and many other western countries for the last 60 years. The CWs has been developed from the 1950s. Sub-surface flow treatment wetlands were developed in Germany in the 1960s through the work of Prof. Kickuth at Kassell University (Conley et al. 1991). Thousands of natural and constructed wetlands across the world are receiving and treating a variety of wastewaters (Kadlec et al. 2000).

The worldwide spread of constructed wetlands started from Europe with pioneer work by Seidel and Kickuth (Max Planck Institute in Plon, Germany) during 1950s (Vymazal 2005). Applications of CWs get momentum during 1980s and started being recognized around the world.

Early development work in the USA commenced in the early 1980s. The Subsurface constructed wetlands using sand and/or gravel, supporting emergent aquatic plants (*Typha*, *Scirpus* and *Phragmites*) were used, calming excellent removal of BOD, TSS, Nitrogen, Phosphorus and more complex organics from wastewater.

Kickuth suggested the use of cohesive soils instead of sand/gravel, using phragmites, in horizontal flow path. According to Kickuth's theory, growth and development of plant roots and rhizomes in soil media will open up the flow channels up to a depth of about 0.6 m. It helps in increasing the hydraulic conductivity of the soil substrate at par with sandy soil (Mucha et al. 2017). Such phenomenon permits a reasonable flow rate through soil media that bears a good adsorptive capacity for phosphorus removal.

North America witnessed its first engineered CW in 1973, that was a pilot system constructed at Brookhaven National Laboratory near Brookhaven, NY. Currently, Florida has many large CWs, like Lakeland and Orlando CWs, started in 1987. Each having an area of 500 hectares for advanced treatment of municipal wastewater. The largest constructed treatment wetland is the 1800-hectare Kiss–Balaton project in Hungarg, started in 1985. The CWs were providing a low cost natural option for water quality improvement in varied climatic conditions worldwide. Although this technology is still somewhat innovative, long-term operational information now exists from many full scales engineered wetlands.

CWs in North America were designed basically to treat large volumes (1 lakh to 15 million gallons per day) of municipal wastewater. A survey of 300 wetlands was conducted in North America, treating primarily municipal wastewater, documented the performance for pollution reduction of BOD (53%), TSS (72%), total nitrogen (53%) and total phosphorous (56%) (Brown and Reed 1994).

In the community of Houghton Lake, located in the Central Lower Peninsula of Michigan (USA), with a population of nearly 5000, the wetland provides additional treatment to the wastewater from STP. The CW system can also promote subsurface through a shallow permeable substratum in which aquatic plants are established (sub-surface flow, SF) (Wood 1995). Sub-surface flow wetlands have received popularity in northern Europe and USA. The attraction towards subsurface system in comparison to free water surface and overland flow systems, was because of their decreased risk of flies and odour nuisance and occupying less area (Reed and Brown 1995). In Europe, the thrust was on application of decentralized CWs for domestic wastewater treatment. Hans Brix a noted plant ecologist of Denmark, who is an authority on CWs, reported that Denmark alone has 150 CWs, mostly in isolated villages treating domestic wastewaters. The use of Reed beds is widespread in northern Europe says Brix. Brix in collaboration with Polish engineers were working in Poland to transfer the technology. Poland developed more than 100 CWs (Brix 1994).

In India in recent past good work is done by National Environmental Engineering Research Institute (NEERI) and Central Pollution Control Board (CPCB), New Delhi. CBCB has developed guidelines and manuals for the constructed wetlands applications. NEERI has developed phytorid technology that has been patented too. A good amount of work has been done in central India with regard to treatment of Municipal Wastewater by sub-surface based constructed wetland (CW) using Phragmites karka as a decentralized system (Prashant et al. 2013).

## 3.5 Classification of Constructed Wetlands

The CWs are classified on several bases, the classifications and the bases are presented in Figure 3.1, despite all sorts of classification (Kadlec and Wallace 2008), the main types are based on the flow direction/pattern.

**Free water surface flow (FWS) wetlands:** This type of CWs resembles very much to the natural wetlands (Fig. 3.2a). In FWS the flow of wastewater is across the media bed. The substratum here is soil layer (35–45 cm). There is a standing water column of 25–45 cm, exposed to the sunlight. The soil layer remains heavily

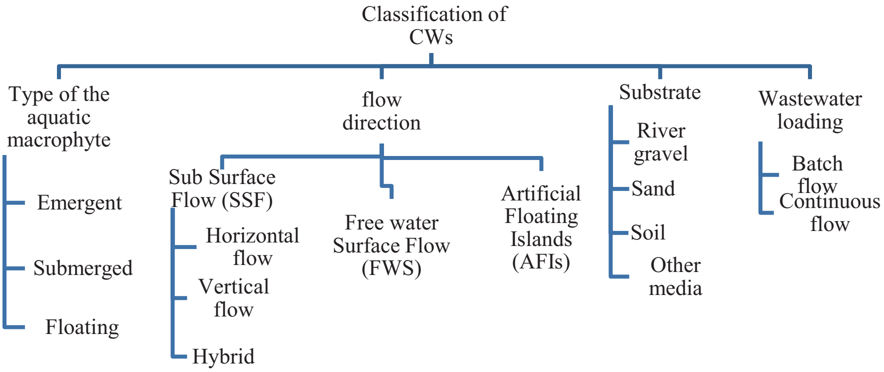

**Fig. 3.1** Types of constructed wetlands

planted with common native macrophytes (*Typha, Phragmites, Scirpus,* etc.). The FWS are used for the tertiary treatment of different kinds of wastewater such as domestic, agricultural, storm water, highway runoff, etc. (Vymazal 2013). The dominant microbial activities mediated by bacteria and fungi are responsible for the treatment of wastewater in FWS. The free waters and the root hair assemblages provide micro-habitats for bacteria and fungi in the wetlands. Here the principal treatment processes are sedimentation, filtration, oxidation, reduction, adsorption and precipitation. Sudden increase in the channel width and standing vegetation reduces the flow velocity thereby enhancing the sedimentation of particles from the wastewater. Major components of FWS are Inlet and outlet arrangements, dykes, berm, soil substrate, impermeable geo textile lining in the bottom (to prevent percolation of wastewater) and emergent macrophytes. The FWS mimic the natural wetlands so, it attracts the wildlife too (Kadlec et al. 2000). The planners choose the FWS mostly for tertiary treatment that receives treated wastewater from activated sludge process trickling filters of lagoons. The nitrification and denitrification processes occurring in aerobic/anaerobic pockets of the CW are responsible for nitrogen removal. Phosphorous (P) is removed via adsorption process, P removal rate is not satisfactory in FWS systems. It a good choice for treatment of low organics wastewater like urban storm water runoff, agricultural runoff, etc. as it also withstands the water fluctuations and flood shocks. The operating costs are low and suitable for all types of climates at lower efficiency during colder periods of the year (Wang et al. 2017). The identifiable feature is water column above the soil substrate. The standing water column attracts the breeding of mosquitos to in tropical/subtropical climate.

**Sub-Surface Flow Constructed wetlands (SSFCW):** The SSFCW has a different flow regime than the FWS, here the wastewater flows below the substrate the supports the vegetative growth. The SSFCW can be classified further into Horizontal Sub-Surface Flow Constructed Wetlands (HSSFCW), Vertical Sub-Surface Flow Constructed Wetlands (VSSFCW), and Hybrid systems.

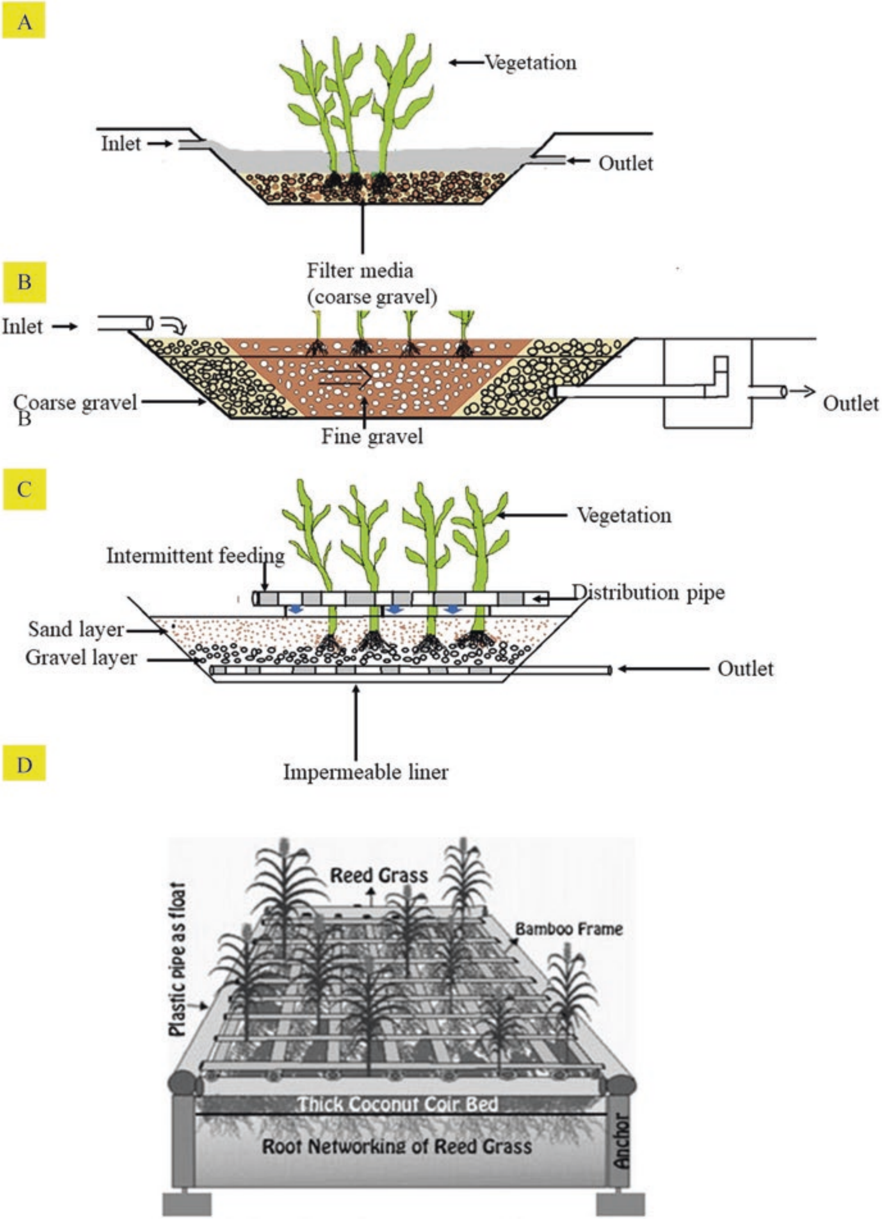

**Fig. 3.2** (**a**) Free water surface flow Constructed Wetlands, (**b**) Horizontal subsurface flow constructed wetlands, (**c**) Vertical subsurface flow constructed wetlands, (**d**) Artificial floating islands

**Horizontal Sub-Surface Flow Constructed Wetlands (HSSFCW):** As the name suggests, in this type of CW the flow of water is parallel to the datum below the substrate (Fig. 3.2b). One can find the water by digging the substrate 5–10 cm deep.

The wastewater flows horizontally through the pores of the filter media (substrate). The wastewater is retained in the CW tankage for a period (hydraulic retention time—HRT) ranging from 24 to 72 h. During the passage of the wastewater from inlet to the outlet it comes into the direct contact with the filter media, biofilm and the roots of the vegetation. The aerobic/anaerobic and facultative pocket of the HSSFCW treats the wastewater by biologically mediated chemical processes (Kadlec et al. 2000). The CW tankage is sealed with impervious strata (clay/geo-membranes) to avoid the possibilities of leakage of wastewater to the below ground. The substrate provides anchorage to the emergent macrophytes. Gravel/sand-based substrates used in these systems have an advantage over the soil-based substrates for better hydraulic conductivity. The HSSFCWs are mostly planted with native aquatic macrophytes such as *Phragmites* (australis, karka, aurundo), *Typha* (latifolia, angustfolia), and *scirpus* (lacustris, californicus). Thickness of the filter media varies between 60 and 80 cm. The vegetation roots and filter media provide space for development of biofilms. From inlet to the outlet zone, a slope is maintained for removal of the treated water from outlet. The outlet system is fitted with mechanism to control the water level below the substrate in the CW. These systems are extensively used for grey water, industrial, municipal and agricultural wastewater treatment. The primary treated wastewater (after removal of suspended solids) is fed to HSFCW in order to avoid the clogging of the filter media/substrate. A screening and sedimentation chamber is pre-requisites for the HSSFCWs. Such types of systems are good for cold climates as here the wastewater is not exposed to the atmosphere. The insulator layer of substrate keeps the water flowing and restrict it from thermal cold shocks. In comparison to the FWS systems the land area requirement is less in HSSFCW, however, the higher capital cost has been reported as a challenge for its application (Kadlec 2009). For better treatment performances these systems have been modified on the basis of its HRTs, wastewater recirculation, batch feeding, ion exchanging filter medias and fluctuating water levels for originating the bed. The applications of HSSFCWs have been reported for several types of wastewaters like industrial, animal husbandry, municipal, storm water and landfill leachates (Billore et al. 2001; Sharma et al. 2013; Lucas et al. 2014; Bakhshoodeh et al. 2020).

**Vertical Flow Constructed Wetlands (VFCW):** VFCWs are the recent addition to the constructed wetlands treatment technology. In VFCWs the wastewater flow direction is top to bottom (perpendicular to the datum) so it is called as vertical flow CW (Fig. 3.2c). It has similarities with the conventional trickling filters. The main components of the VCFWs are the tankage, substrate (filter media), inlet and outlet arrangements, sealing material like geo-membranes and emergent macrophytes. The arrangement is made in a closed vessel usually above ground. The vessel is filled with the graded filter media (sand and/or gravel). The depth of filter media varies from 30 to 180 cm (Brix and Arias 2005; Vymazal 2014). The filter media is arranged on the basis of its size, the lower part is filled with comparatively bigger size gravel and the upper part contains the smaller size sand/gravel. This arrangement of the filter media shall be done keeping in consideration of hydraulic conductivity and short circuiting of the flow. If not arranged properly, small channels may develop from top to bottom within the filter media for vertical the passage of the wastewater and even distribution of the wastewater throughout the filter bed is compromised. The top of the VFCWs is planted with suitable emergent macrophytes (mostly *Phragmites and Typha*) (Calheiros et al. 2009). The wastewater is applied on the top surface of the VFCWs through perforated pipes. At the bottom of the tankage, a network of perforated pipes is laid and connected to a single outlet for removal of the treated water. A provision of forced aeration through vertical perforated pipes is also applied keeping the system in aerobic mode (Stefanakis and Tsihrintzis 2012). The tankage is made watertight by applying the geo-membranes at the bottom and side walls of the VFCWs. A slope of 1–2% towards the outlet holds good for efficient collection of the treated water at the outlet. The VFCWs functions in aerobic process for the degradation of organics present in the wastewater. The aerobic condition is maintained by batch application of the wastewater, between two cycles of the application of wastewater, the substrate gets refilled with the air into its pores. This condition supports the vigorous microbial mediated nitrification of the constituents of wastewater (Platzer 1999). A pre-treatment of wastewater for removal of the suspended solids is recommended to avoid the clogging of the filter bed. The VFCWs exhibit a god removal of suspended solids, biodegradables organics and ammonia. Due to the presence of air in the pores VFCWs are efficient on $BOD_5$ removal (Cooper 2005). The phosphorous removal efficiency is at lower side that may be enhanced by mixing certain media having high adsorption capacities (Brix et al. 2001). These are the compact systems and require lesser area in comparison to the FWS and HSSFCWs but high manual supervision for its maintenance (Stefanakis et al. 2014). The application is mostly reported for purification of domestic wastewater; still it is used for treatment of landfill leachates, dairy effluents and airport runoffs (Branchu et al. 2014; Pelissari et al. 2014; Bakhshoodeh et al. 2020).

**Artificial Floating Islands (AFIs):** AFIs or Artificial Floating Reed Beds (AFRB) are a new alternative to CWs meant for onsite treatment of water bodies (Billore et al. 2009). The AFIs evolved on the principal of CWs and natural floating islands that are similar to hydroponics. Free-floating aquatic plants or sediment-rooted emergent riparian vegetation in subsurface flow or surface flow CWs were the traditional land based designs. The AFIs are recent edition of CW, here rooted emergent plants (reed, typha, etc.) are grown on a floating mat over water surface rather than rooted in the sediments (Fig. 3.2d). The floating features of AFIs amid the water column make them suitable for in situ treatment applications, without being affected by the fluctuating water column of lakes or reservoirs. The AFIs are designed in a way that the roots of the vegetative mat hang in the water column for a depth of at least 0.75–0.80 m. The Eco-engineered Artificial Floating Islands (AFIs) are initiative in the area of onsite treatment of degrading freshwater systems including ponds, lakes, reservoirs, stagnant rivers, artificial lagoons or oxidation ponds.

AFIs are floating superstructures composing emergent plants specially reed (*Phragmites karka*) (Billore et al. 2009) floating on waterscape. The major components of the AFIs are floating mat usually made up of coconut coir, bamboo pieces, emergent macrophytes and floats (Prashant and Billore 2020). The AFIs remove the pollutants from open water surface through nutrient uptake from macrophytes, sedimentation process, root attached particulate matter (RAPM) accumulation and microbial activities (Wang et al. 2020). The AFIs has been applied for the removal of pollutants from storm waters (Headley and Tanner 2012) and for aesthetic purposes.

**Hybrid Constructed wetlands:** This type of wetlands are combination of both horizontal flow type and vertical flow type CWs. The purpose of the combination is to achieve the high degree of treatment of the wastewater. The uniqueness of HSSFCW and VFCW combination gives a better result for $NH_4$–N and Total Nitrogen removal (Vymazal 2005). These CWs have also better treatment efficiency for BOD, COD, suspended solid, pathogens, heavy metals and also for the emerging pollutants (Masi and Martinuzzi 2007). Successful treatment of variety of wastewater, such as dairy (Sharma et al. 2013), leachate treatment (Saeed et al. 2021) has been reported from the hybrid CWs. Some disadvantages are embedded with this treatment system like large area demand, more complex design mechanism and difficulty in working in cold climate.

**Components of the Constructed wetlands:** Major components of the constructed wetlands that play important role in the treatment of wastewater are the filter media/ substrate and vegetation (Wu et al. 2015).

**Media for Constructed wetland:** Substrate media means the filter which is used to trap significant pollutant in sewage through various treatment processes. These processes are sedimentation, filtration, adsorption, etc. Substrate media provides a path through which wastewater can flow and surface on which microbes can live. These microbes feed on waste material present in wastewater and remove them. Surface type and size of substrate provides the special site for biofilm development and adsorption of nutrients too. The physical and chemical property of substrate media can affect the treatment efficiency of whole CW system. If the filter media is made up of porous material having large surface area, then it can improve the hydraulic and mechanical property of treatment system. The hydraulic conductivity of the media is a key parameter in deciding the performance of CW system (Sundaravadivel and Vigneswaran 2001). Hydraulic retention time depends on it. The particle size distribution is the main parameter that influences the soil hydraulics (Stottmeister et al. 2003). According to previous study fine sand and soil-based substrates have less hydraulic conductivity while coarse substrates (sand/gravel) have high conductivity. The substrate media plays a significant role in nutrient removal mechanism also (Prochaska and Zouboulis 2006). Adsorption is the key process for the removal of the phosphorous which occurs through the filter media. In $N_2$ removal mechanism, substrate media plays an important role also. Nitrification–denitrification reaction is the main $N_2$—removal procedure. For these reactions the possible microbial environment can be possible in suitable filter media (Reddy and

**Table 3.1** Role of media in wastewater treatment under CWs

| Sl No. | Treatment processes | Role of media |
|---|---|---|
| 1 | Filtration | In this process substrate media particles provide pore spaces for the trapping of suspended materials present in the wastewater |
| 2 | Sedimentation | In this process the settling of suspended particles occurs as it passes through the substrate media. These particles accumulate in the bottom surface of wetland medium |
| 3 | Nitrification | In this process the conversion of ammonia to nitrate in aerobic condition (presence of $O_2$ which is present in the upper portion of wetland media) |
| 4 | De-nitrification | In this process the conversion of nitrate to nitrogen gas under anoxic condition around the lower part of wetland media |
| 5 | Adsorption | In this process the removal of pollutants through attachment to the surface of media and biofilm. Biofilm develops on the surface of media and around the plant root |
| 6 | Assimilation | In this process the incorporation of wastewater pollutants into microbes and vegetation those are growing on the surface of media |

D'Angelo 1997). The role of filter media in governing the various treatment processes are mentioned in Table 3.1.

The media is very essential and growth and development of the vegetation. The type and size of the media is an important consideration. The size of the media particles can affect the ability of treatment of the CW.

- Substrate media particle of small size has small pores. These small pores can filter smaller particles from the wastewater effluent.
- With large surface area of media particle, large amount of microbial assemblage can be possible which enhances the degradation of waste materials present in effluent.
- Large media particles have good ability to reduce transmission of odours and vectors (disease causing). These large media particles have large openings that allow better air exchange which can allow the exit bad odour and vectors too.
- The media particles should be off suitable size because very small sized particle can cause the clogging problem more often and extra-large particle can allow the wastewater to flow through the bed without proper treatment.

**Characteristics of different media particle used in CW**

- *Bulk porosity*—It is the amount of space between media particles. These spaces are filled with air or water. The bulk porosity should be about 30% which allows the wastewater to flow adequately through the wetland media. This amount of porosity provides sufficient time to the effluent for the better contact with media particle.
- *Stability*—The media should be made up of such kind of particle which are strong enough for their long-time stability.

- *Particle size*—The media particles should be off suitable size because very small sized particle can cause the clogging problem more often and extra-large particle can allow the wastewater to flow through the bed without proper treatment.
- *Surface area*—With large surface area of media particle, large amount of microbial assemblage can be possible which enhances the degradation of waste materials present in effluent.
- *Uniformity*—The particle size along the whole media surface should be same. With similar size of particles, the pore size between them is also same, which maintain the uniform permeability throughout the media surface.

## 3.6 Frequently Used Media

The sand, gravel and soil are the commonly used filter media in many CWs. Sand is readily available in the nearby rivers and construction material suppliers. Soil substrates helps in ammonia removal through interaction with the strata, humic substances (Kadlec 2009). The peanut size gravel is the most suitable media in the CWs. Now a days alternative media is also being used into CWs. The major classes of the alternative media are natural (zeolite, limestone, bauxite, etc.) artificial/by products of industries (coal fly ash, red mud and slag etc.) and man-made products (light weight aggregates) (Valipour and Ahn 2016). The role of substrate in phosphorous and nitrogen removal is presented in Table 3.2.

**Vegetation for Constructed Wetlands:** The wetland vegetation is an essential component of the CWs that play key role in treatment of wastewater. The major classes of the vegetation used in CWs are emergent macrophytes, submerged vegetation, floating plants. Important functions of the vegetation are to stabilize the surface of filter media, manage the suitable condition for filtration process, provide large surface area for microbial assemblage, biofilm development for better degradation of wastewater and translocation of the oxygen to the gravel bed (Brix 1997). The wetlands vegetation shall be selected on the basis of certain properties.

- The vegetation shall not be a weed into the area of reason for any disease.
- It shall be a locally available ecologically acceptable vegetation.
- It shall be tolerant to the high organic and nutrient loads.
- The pollutant removal capacity shall be high.
- Vegetation should have large sized roots and rhizomes for providing large space for microbial assemblage and for oxygenation process.
- Vegetation should have high aboveground cover for insulation during winters.

**Major role of vegetation in CWs:** The presence of vegetation reduces the flow velocity of effluent into the CW, which creates better condition for the sedimentation process (Persson et al. 1999). It also stabilizes the substrate media through compact binding of media particle with the help of their root system. In temperate areas the vegetation covers provides insulation cover to the wetland surface and

**Table 3.2** Comparison of different filter media for removal of phosphorous and nitrogen

| Filter media | Phosphorous removal | Nitrogen removal | References |
|---|---|---|---|
| Gravel and Gravel-soil | Very good | Much less | Smol et al. (2015) |
| Zeolite and Zeolite-limestone | Less | Very good | Hussain et al. (2011) |
| Fly ash | Very good | Very good | Vohla et al. (2011) |
| Zeolite | Less | Very good | Zhang et al. (2014) |

keep the media substance free of frost during winter season. The roots and rhizomes of macrophytes provide the water channel through the soil pore in the substrate media which maintain the conductivity of wastewater through it. The roots and rhizomes of macrophytes enhance the loosening of soil and after their death they leave the tubular pores and channels made by them. Therefore, they not only maintain the hydraulic conductivity but also stabilize it. Vegetation in CW enhances the concentration $O_2$ in the wetland environment by leaking $O_2$ into it. The rate of leakage of $O_2$ is highest in the root region. The rich oxygen environment helps in oxidation of the harmful pollutants in the rhizosphere and supporting nitrification process. Macrophytes used in CW have large root system, which provide the rhizosphere, centre of microbial activity. It enhances the microbial density and activity by increased root surface for their growth. These grown microbes are responsible for the degradation of wastewater pollutants. Therefore, by enhancing the surface area, macrophytes help in the treatment process, the sole purpose of CW. Like other plants wetland plants also require nutrients for their growth. They take nutrients through their root system. In CW, wastewater effluent has large amount of nutrient concentration in the form of nitrate and phosphate compound. Macrophytes take these nutrients for their growth and reproduction and make the effluent nutrient free. The uptake of nutrient is stored as plant biomass (Brix 2003). Macrophytes not only uptake nutrients but also heavy metals and other harmful chemical compound present in wastewater effluent. These are accumulated into different plant parts like stem, leaves, etc. Different parts of the macrophytes have been recognized to play some particular functions. The aerial plant tissues of the vegetation attenuate sun light and reduce the growth of algae that cause clagging in the inlet and outlet regions. It also provides insulation to the bed. It has an aesthetic appearance apart from the main role of nutrient storage. The plant tissue that remains present in the water helps in filtration by removing larger debris, reduce the flow velocity thereby increasing the rate of sedimentation, providing space for growth of surface attached microorganisms, nutrient uptake and photosynthesis. The submerged part includes the roots and rhizome that has special role in preventing the erosion of substrate, release of oxygen into the bed, nutrient uptake and release of root antibiotics.

**Siting criteria and design consideration of the CWs:** The siting of the full-scale field level CWs and the design criteria is an important aspect, beforehand the actual installation of the CWs.

- Location and size of the land: A decentralized system shall be adopted and the site of constructed shall be close to the wastewater generation point. The commercial lands shall be avoided to keep the cost low. The strategic location helps in developing a green patch for aesthetic look. The location shall be easily approachable. There shall be a reuse plan of the treated water or availability of the water bodies for final disposal of the treated water. A natural gradient from the points of wastewater generation and CWs location is favourable, in order to avoid the usage of pumps for lifting the wastewater. The size of the CW depends on the quantity of wastewater to be treated, pollution load of the wastewater and desired quality of treatment. The most common criteria for the sizing, is unit area required ($m^2$) per person equivalent (PE). Before designing one must learn what are the legal compliance/treated water quality standards of the local government. Major heads for the cost estimation of the CWs are as follows.
- Size and per unit price of the land.
- Development of sewerage system (civil work).
- Requirement of pumps (capacity and unit price).
- Excavation of the land for preparing the tankage.
- Volume of the filter media to be filled in the tankage and unit volume price.
- Area of the sealing material (geo-membrane/LDPE liner) required and unit area price.
- Plant material: the native vegetation is grown in nursery then planed in the CWs. Usually, such plants are not commercially available in the local market. The cost of plant material preparation involves nursery development, polybags for the growth of saplings, sand and soil mixture to be filed in the poly bags and irrigation for the growth of the plants.
- Skilled and semiskilled labours requirement for tank excavation (can be done by machines also), nursery work, filling substrate into the tankage, etc. can be hired on the man days basis.

**Design criteria for HSSFCWs:** The HSSFCWs are the secondary wastewater treatment process that focus on BOD and TSS removals. Usually, the pollutant removal efficiency for BOD and TSS varies from 60 to 85% and 60 to 90%, respectively (Vymazal and Kröpfelová 2009; Prashant et al. 2013). Type of the wastewater, pollutants concentration and hydraulic retention period of the CWs are the critical parameters to decide the efficiency. Due to the presence of anaerobic zones in the bed, the HSSFCWs are efficient in de-nitrification. Many workers have put forward the sizing/design guidelines that vary from place to place depending on the local climatic conditions, local materials and plants. The specific surface area requirement method is most comfortable one keeping the depth around 0.6–0.8 m. The population equivalent (PE) is a guiding factor for determining the size of CW. The PE is the ratio of total BOD (kg/day) and per capita BOD (kg/day). In a Czech Republic review the population equivalent was reported between 4 and 1200 (Vymazal 2002). For Indian conditions the average daily per person BOD load is considered 45 g for the estimation of population equivalent. The studies carried out in Denmark and UK evaluated that for pre-treated wastewater size of HSSFCW has value of about 5 $m^2$/PE (Vymazal 2002). A length and width ratio of 2:1 is ideal for secondary treatment; it helps to maximize the cross-sectional area of flow and minimize clogging problems. The vegetation root penetration is around 0.6 m so ideally the depth of filter media is kept as same. A simpler way of sizing the HSSFCW bed can also be done one the basis of porosity ($\eta$) of filter media, HRT (time in days), and discharge ($Q$= $m^3$/day) (Billore et al. 1999). Based on the $BOD_5$ concentration and inlet ($C_{in}$—mg/L), desired $BOD_5$ concentration at the outlet ($C_{out}$—mg/L) average flow rate per day ($Q_d$—$m^3$/day), the size ($A_h$—$m^2$) of the HSSFCW is determined by the equation ($A_h = Q_d$ (ln $C_{in}$ − ln $C_{out}$)/$K_{BOD}$) for pre-treated domestic wastewater where $K_{BOD}$ is the rate constant ($day^{-1}$) (Kickuth 1977).

**Design criteria for VFCWs:** The vertical flow (VF) systems require less area in comparison to the HSSFCWs. The parameters for designing of the VF systems are very much similar to the horizontal flow systems. The population equivalent is the most commonly (many national guidelines are suggested) used parameter for the sizing of the VFCWs. Apart from the population equivalent (PE), the daily organic load (gBOD 5/$m^2$ day or gCOD/$m^2$ day) can also be used. The reported PE for VFCW range from 1.2 to 5 $m^2$/PE (Brix and Arias 2005; Kadlec and Wallace 2008; Molle et al. 2008).

**Pre-treatment:** The secondary treatment based CWs shall receive pre-treated wastewater. Here the meaning of pre-treatment is removal of suspended particulate materials, floating substances and removal of oil and grease. Insufficient pre-treatment cause clogging of the VFCWs and HSSFCWs. Based on the characteristics of the wastewater, the pre-treatments like screens, sedimentation tanks, grit removal basins and skimming tanks may be selected. For the municipal wastewater, the effluents of the anaerobic pre-treatments (septic tanks, imhoff tanks, baffle reactors, etc.) can also be fed to the CWs.

**Inlet and outlet arrangements:** The inlet of the CWs is important as it governs the flow distribution of the water in the wetland cell. A proper inlet arrangement helps in avoiding the short circuiting of the flow from inlet to the outlet. The inlet and outlet structures of the surface flow wetlands/free water surface flow wetlands are simple, just to release the water in the cell and collect it from the cell. But in subsurface flow systems (HSSFWs and VFCWs) uniform distribution across the filter media is essential for better treatment. A higher length-width ration (3:1 or more) supports uniform flow distribution. The inlet is kept above the filter media for proper distribution, cleaning and maintenance of the inlet. The inlets can be termed as, single point inlet, spreader trench or perforated horizontal pipe along the width. Provision of water sample collection shall be there for monitoring and analysis. The perforated inlet pipe above the filter media is exposed to the sunlight that causes development of algae in the orifices. An inlet perforated pipe covered with the filter media reduce the chances of development of algal slimy layer. Coarse filter media or bigger size gravel/stone shall be used at the inlet for proper distribution of the wastewater being fed.

The outlet arrangement functions mainly (1) to collect the treated water from the distal end of the CWs, (2) to control the water level in the wetlands and (3) to provide a point for sample collection. In HSSFCWs a perforated pipe is laid at the bottom of the distal end along the width of the cell. An arrangement shall be provided at the outlet to adjust the water level in the CW bed. At the outlet zone again larger/coarser filter material shall be placed for better hydraulic conductivity. A good slope (1%) from inlet to outlet is required. Shade shall be provided at the outlet/treated water collection well shall minimize algal growth by cutting light. In VFCWs a network of perforated pipes shall be laid at the bottom surface of the cell for efficient collection of the treated water.

**Sealing of the cell/tankage:** The wastewater fed to the CW bed shall remain into the cell itself. There shall not be leakage of the wastewater into the ground water. Otherwise, the purpose will be defeated if the wastewater percolates and meets to the groundwater. To make the CW cell impervious mostly geo-membrane/LDPE liners are laid to the bottom or sides of the wetlands. After excavation of the tank the following shall be done (in case of HSSFCWs) to make the cell water tight:

- Clear all the pointed stones from the excavated cell bottom and sides.
- Clear all the pointed roots, stems that may pierce the liners.
- Remove the water logging if any.
- Provide a layer of cushion (sand) at the bottom.
- Lay the LDPE liners.
- Interlock and seal the liner with other pieces.
- Seal the liners with the native soil at the top of the cell.
- After laying the impervious layer, filter media shall be filled in the cell.

**Vegetation development and plantation:** Vegetation is an important component of CWs, it plays a vital role in oxygen transport, nutrient uptake, biomass accumulation and microbial growth in the rhizosphere (Chen et al. 2016). In a CW planning and design establishment of vegetation is very important stage. The various steps of establishment of vegetation include the following.

- Selection of plant species.
- The plant species shall be selected on the basis of the local availability of the plant species, wastewater to be treated, rapid growth, dense root system.
- Looking for such plant species stock on nearby water bodies.
- Development of vegetation in nursery.
- Planting the saplings in the CW bed.
- Decide number of plants/$m^2$ (usually 4/$m^2$).
- Impound the CW bed with water for few days for vegetation growth.

**Operation and maintenance:** The CWs are designed with a focus with minimum maintenance but all the CWs require some timely maintenance for proper functioning of the CWs. The objectives of operation and maintenance are as follows.

- To validate that the CWs are working as per the design.
- To increase the treatment efficiency.
- To increase the life of the CWs.
- To save cost of the major breakdowns.

The major operation and maintenance issues of concern are regular flow of the water in the bed, maintaining the level of water, maintaining the vegetation cover, regular sampling, monitoring and analysis.

The major problem being faced by the operators/investigators are the clogging of the bed of CWs. The clogging occurs when the pores of the filter media get filled by the solids being bought by the wastewater and the death of the vegetation. Due to the clogging of the bed the waste capacity of the CW decreases. The domestic wastewater contains sizable amount of the suspended solids that need to be removed beforehand feeding to the CW. Usually the maintenance of the septic tank and the sedimentation tanks are compromised that results in feeding high suspended solids laden wastewater in the CWs. CWs shall not be considered as the primary treatment units. Properly washed filter media shall be filled in the tank of the CWs. The filter media needs to be inspected on the regular basis to ensure that clogging is not there. If the clogging has occurred and flow is being interrupted, then the operator shall see for the replacement of the filter media.

Hydraulic stress: Sometimes the CWs are designed for the higher capacities of treatment but starts operating at the low quantities of wastewater. In that case the water level remains below the root penetration causing death of vegetation. Such issues can be easily solved by raising the outlet weir or by adding more wastewater into the cells.

Flooding: sometimes due to heavy rainfall flooding occurs in the bed. The storm water through the drains and surface run off comes to the CW bed. The flooding causes loss of vegetation and clogging of the bed. Such scenarios may be avoided by provision of bypass channels before the inlet point at the same times dykes around the CW bed will restrict the entry of runoff to the bed from nearby areas.

De-weeding: the weeds (that are not a planned vegetation in the CW) shall be removed on the regular basis, especially at the initial period. The weeds compete with the vegetation in focus and efficiency of CW decreases.

Temperature: CWs are nature-based wastewater treatment system. Like natural wetland, these are also exposed to atmosphere, thus affected by temperature. Temperature variation also affects the treatment efficiency of the CW. The treatment efficiency of CWs differ in summer and winter season, affecting the water quality parameters like TSS, BOD, TP TN, etc. and both biological and physical activities of the wetland system (Kadlec 2006). The treatment performance of wetland is seasonally cyclic and the biotic reactions are reduced at temperature lower than the optimum range 20–35 °C (Kadlec and Reddy 2001).

## 3.7 Treatment Mechanism of CWs

The treatment mechanisms identified in CWs are classified physical and biological processes. The CWs perform better than the conventional treatment systems due to the process of biodegradation, photo degradation and plant uptake (Matamoros et al. 2010). The main pollution removal mechanism is presented in Table 3.3.

**Physical processes**

- Sedimentation and filtration are two main processes included in the physical treatment of wastewater. The process sedimentation works on the principal of gravity in which the settling of suspended particle is done according to their shape, size and mass. It is the part of primary treatment of wastewater in which a sedimentation tank is added to the CW system. In this sedimentation tank large particulate matters settle down due to the gravitational settling. The process sedimentation is mainly used for the removal of suspended solid from the wastewater effluent and it also helps in reducing the clogging problem. Apart from the primary treatment sedimentation also occurs in the CWs, the sudden increase into the cross-sectional area at the entry point of wastewater causes reduction in the flow velocity causing sedimentation of the suspended particles.
- Filtration is the physical process in which particulate matters are filtered mechanically when wastewater pass through substrate and root masses. In this process small sized particulate matters adsorbed on the substrate or trapped in root masses (Dotro et al. 2015).

**Chemical processes**

- Adsorption, precipitation and chelation are the major chemical processes of the CWs. Phyto-volatilization and Phyto stabilization are other important chemical process used for the removal of heavy metals and other emerging pollutants.
- Adsorption is the process of deposition and retention of dissolved substances on the surface of substrate media. It is main process responsible for the phosphorous removal from the wastewater (Lin et al. 2008). Heavy metals are also removed by this process. In the removal of heavy metal their adsorption occurs on organic matter present in substrate media and wastewater. Ammonium cation ($NH_4$+) also gets adsorbed to the surface of filter media due to their charged property.
- Precipitation is the process of wastewater treatment in which the formation of co-precipitant with insoluble compounds occurs and due to gravity, they are precipitated to the bottom of treatment system. It depends on the solubility of metals, wastewater pH, metal ion concentrations and significant anions.
- Chelation is the chemical process of wastewater treatment in which a reaction takes place between a metal ion and an organic pollutant, which results in the formation of a ring structure that encompasses the metal ion and removes it. It helps in the removal of heavy metal present in the wastewater.

**Biological processes**

- Ammonification, nitrification and denitrification are the three main biological processes involved in wastewater treatment in CW. Some other processes are also involved in it like photosynthesis, fermentation, microbial removal, etc.
- In ammonification process organic nitrogen is converted into $NH_4^+$–N (Vymazal 2007). In ammonification process the deamination reaction of amino acid takes place which results to the formation of $NH_3$. The rate of this reaction is high in the upper portion of CW due to the aerobic condition. But in the lower portion the rate of ammonification reaction is low due to the partial anaerobic environment (Reddy et al. 1984). The rate of ammonification reaction also depends on the pH and temperature. The optimum pH for the ammonification reaction is 6.5–6.8.
- In the biological treatment process of wastewater, the nitrification occurs in two steps. These two steps involve first the conversion of $NH_4$–N to $NO_2$–N and the second is the conversion of $NO_2$–N into $NO_3$–N. The first step takes place in the upper portion of CW due to the requirement of aerobic environment. Some microbes are involved in the first step reaction like nitrosomonas, nitrococcus. The second step of reaction also takes place with the help of microbes like nitrobactor.
- Denitrification is the process of total nitrogen removal form wastewater in constructed wetland (Koottatep and Polprasert 1997). In this process the conversion of nitrate into nitrogen gas occurs. It needs the anaerobic environment for the smooth generation of nitrogen gas. Therefore, in VFCW the poor denitrification process occurs due to the high concentration of oxygen. Various bacteria are involved in denitrification process such as Bacillus, Enterobacter, Micrococcus, Pseudomonas, etc. (Ottová et al. 1997).
- Some other biological processes also help the treatment mechanism of CW like photosynthesis, fermentation, etc. Photosynthesis influence C and $O_2$ addition to the wetland. Both C and $O_2$ run the process of nitrification. Fermentation is the anaerobic decomposition of organic carbon and produce compounds like volatile fatty acid. These compounds are of high energy value which is used in microbial degradation process of wastewater.

**Table 3.3** Pollutant removal mechanism under constructed wetlands

| Pollutants | Removal processes |
|---|---|
| (BOD/COD) | Sedimentation, biological decay, microbial transformations/uptake |
| Solids | Sedimentation, adsorption, filtration |
| Nitrogen | Nitrification/de-nitrification, plant/microbial uptake and volatilization |
| Phosphorus | Matrix sorption, plant uptake (substratum adsorption, chemical precipitation, bacterial action) |
| DO | Gaseous exchange |
| Total coliform | Sedimentation, UV radiation, antibiotics as root exudates |
| Metals | Adsorption, microbial oxidation/reduction, precipitation, plant uptake (partial) |

## 3.8 Advantages and Disadvantages

The advantages of the CWs are counted over the conventional wastewater treatment systems. The CWs need fewer mechanical parts as the major role for treatment is played by the vegetation and media. The operational cost of CWs is also low in comparison to the conventional system. The CWs operate on solar energy (Not PVC), so requirement of conventional energy is low. High volume of sludge is produced in the conventional systems as a by-product, in case of CWs the sludge is not produced in the secondary treatment process. It also provides additional advantages as habitat for birds, wildlife and macroinvertebrates (Prashant and Billore 2020). The appearance of CWs also looks good. At the same time the land area required for the establishment of CWs are high. The treatment capacity changes from place to place as these are natural systems so, the variation in the climatic condition has an effect on it. In conventional treatment process the microbial activity is under control but that is lacking in the CWs.

**Conclusion:** CW's getting popularity as a substitute to traditional wastewater treatment systems. These provide a sustainable decentralized solution for isolated communities, small cities, countryside, individual houses, housing society, that are not connected to wastewater collection and treatment systems. It exhibits multiple benefits that actually need to be analysed in economic terms too, like habitat for birds and wildlife, good scenic beauty, recreational purposes, potential of reuse of treated water for irrigation in nearby areas. In general, CWs are easy to construct, simple to run and offer better treatment efficiency. The CWs are being seen as sustainable systems, providing sanitation, protecting environment and water resources. The CWs have been proved good for domestic wastewater treatment. There is an urgent need to scale up the application of CWs. Environmental entrepreneurs shall look forward to adopt the tested technology for field applications, as well as the certifications and third-party evaluation of the established CWs shall be carried out.

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# Chapter 4
# Membrane-Based Remediation of Wastewater

**Manoj Chandra Garg and Harshita Jain**

**Abstract** Contamination of water resources has an overall impact and is a cause of worldwide concern because of which requirement for clean water is getting increasing. Membrane-based wastewater treatment technology may uphold effective techniques for the treatment, utilization, and reuse of water and the improvement of next-generation water supply frameworks. With progress in membrane filtration techniques, various sorts of membrane are arising for applications in water filtration and wastewater treatment technologies owing to their viability against both synthetic and natural toxins. This chapter discusses the utilization and applications of membrane filtration techniques that are being assessed or created as option for water treatment. Membrane filtration techniques are inherently preferable in terms of performance over different treatment techniques utilized in water purification on account of their high surface area, lower energy consumption, and high performance. Owing to these attributes, these might be utilized in future at large scale for water treatment.

**Keywords** Water treatment · Wastewater · Membrane technology · Biofilm · Nanomaterial

## 4.1 Introduction

Worldwide water assets are deficient in fulfilling the potable water needs of mankind. Rapid industrialization, changes in the environment, and other human exercises have additionally demolished the situation. In this regard, water reuse has turned into a broadly acknowledged way to deal with supporting the water supply (Elbasiouny et al. 2021). Wastewater treatment has for quite some time been executed to supply clean water and backing financial turn of events. Different types of

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customary innovations, for example, adsorption and coagulation are being customarily utilized to a huge extent. Desalination is the most common way of desalting water and is a rising innovation for resolving problems identified with water lack and contamination. The process of desalination is performed either thermally or through membrane-based treatments. At present, thermal-based membrane processes are generally utilized in numerous provinces which are under water stress, especially in Middle Eastern locales. A positive shift from these traditional innovations to the utilization of membrane advances has been observed due to its wider industrial and environmental applications. The expanding acknowledgment of membrane process in the desalination and treatment of water and wastewater is primarily a result of the capacity of membrane innovation for dealing with a wide scope of feed water having high functional dependability. Technologies based on membranes are additionally equipped for delivering water and freshwater that is of excellent quality concerning the expulsion of microorganisms, broken down particles, and suspended solids (Khulbe and Matsuura 2018).

Membrane technology also has other advantages, such as its compact footprint and versatility and could be effortlessly backfit in existing arrangement to provide a synergistic effect to ease the filtration process. Membrane performance can be improved with breakthroughs in the production of polymer and ceramic based membranes, allowing them to manage numerous developing contaminants that are too difficult for current treatment techniques (Rongwong et al. 2018). Membrane separation is essentially the process of separating unwanted contaminants and allowing pure water passage through selectively porous membrane. Desalination and wastewater can be divided into numerous membrane techniques on the basis of other factors including driving force and finite element analysis.

Membrane technology is divided into two types of processes: pressure-driven and osmotically-driven. Pressure is applied to the feed side of the membrane in the former process, which functions as a means of propulsion for separating contaminated incoming feed water into permeate having pure water and concentrate having impurities that is generally discarded/processed further (Shukla et al. 2021). Reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration are the most prevalent pressure-driven membrane processes (MF). The natural osmotic gradient is the driving force in non-pressure driven membrane processes like forward osmosis (FO) and pressure-retarded osmosis (PRO). Filtration is propelled by osmotic pressure that is produced naturally. FO and PRO have grown in prominence as an alternative to traditional membrane techniques which employ excessive external pressure and waste a lot of energy while maintaining great water quality and production (Algieri et al. 2021). Fabrication of membrane and its structure design are two of the most significant tactics for ensuring membrane technology's efficiency and long-term viability. Efforts have been made to improve membrane performance using a variety of methods which includes the utilization of innovative and smart materials for fabrication, also the insertion of novel nanostructures and additives and the synthesis of a novel membranes which reveal aspects of traditional separation technology to accomplish pollutant removal synergy (Shukla et al. 2021). Such strategies are helping in the development of ideal membrane design and production techniques that outperform those now in use. Strong rejection capability; great chemical, physical, mechanical, and thermal stability; extreme resilience to harsh chemicals; strong integrity towards wide pH and temperature range are just a few of the benefits of these membranes.

This chapter gives an overview of membrane technology's unique and long-term development in wastewater treatment and desalination. The first section discusses membrane processes based on hydraulic and osmotic pressure. The evolution and progress of high-performance membrane design and fabrication are discussed. Membrane technologies are discussed in terms of desalination and treatment of wastewater treatment. Finally, the innovative and sustainable membrane techniques are addressed briefly and conclusions are reached.

## 4.2 Membrane-Based Techniques

### *4.2.1 Pressure-Assisted Membrane Techniques*

The pressure-driven membrane processes utilize membranes as a barrier preventing undesired chemicals from passing through while enabling water to pass through. The propulsion that causes liquid to pass through the membrane holes is the pressure differential among the incoming and outgoing water. Unwanted chemicals are kept because of physical properties like charges, size, and shape (Homaeigohar and Elbahri 2017). Pressure-driven membrane processes can be classified into four categories based on retained particles size, i.e., RO, MF, NF, and UF. The largest pore size is of MF membranes (0.1–10 mm) with least applied pressure range among these techniques. MF membranes have a large pore size, which allows for great permeability at low pressure. In comparison to MF membranes, pore size of UF membrane is 2–100 nm with lower permeability and high applied pressure (Govardhan et al. 2020). The pressure range of UF is typically 1–10 bars. In both MF and UF, sieving is the primary method for successfully separating suspended particles, colloids, and microorganisms. MF and UF are often employed as a pretreatment in many membrane separation procedures to eliminate or decrease contaminants which causes difficulties in treatment techniques like NF and RO. With the pore range of 1 nm, NF possesses characteristics that fall between UF and RO (Koyuncu et al. 2015). Minute contaminants like dyes and organic biological particles can be removed by NF. Size exclusion and surface charge methods are used to separate NF. The ionization of carboxylic group and sulfonic group causes the membrane surface containing these functional groups to become mildly charged when exposed to aqueous solutions. They possess acidic or basic characteristics depending on the materials utilized. Since, NF membranes can be used to separate divalent ions, they are also known as loose RO membranes. As a result, NF has been used in water softening and desalination. For typical divalent ions like magnesium and calcium, NF can provide up to 95% rejection. With regard to filtration mechanisms, NF filtration is not only established on size exclusion but also Donnan and dielectric effects. In that the surface charges and charge particle diffusion play a role in rejecting ionic compounds (Ahsan and Imteaz 2019; Chuntanalerg et al. 2019).

NF and RO have a few things in common: they are both utilized to eliminate dissolved particles and need a lot of external hydraulic pressure to work. Membrane materials and configurations are also similar in NF and RO (Semiat 2010). In comparison to RO, nanofiltration has a better water productivity, whereas uses less specific energy. NF, on the other hand, only demonstrates rejection in the 50–80% range for monovalent ion separation. The separation of salts and microorganisms by membranes utilizing greater external pressure than natural osmotic pressure is what RO is all about. The desalination of seawater and brackish water is the most prevalent application of RO. Reverse osmosis has surpassed thermal desalination methods like multistage flash distillation (MFD) to turn out the most widely used desalination method. The salt rejection effectiveness of RO is up to 99.9% sodium chloride (NaCl) removal. Due to the subnanometer range of the RO membrane pores, RO can provide a nearly unbroken barrier for pathogen elimination (Ismail et al. 2019). As a result, RO is utilized in the treatment of wastewater for reusing water. The widespread utilization of RO process on a global scale is largely due to major advancements in process optimization and membrane fabrication, which has resulted in lower operational costs. The improvement in membrane flux has resulted in a significant reduction in energy usage as a result of these developments. Cleaning and membrane replacement expenses are also reduced as a result of the fabrication of more robust membranes.

### *4.2.2 Non-pressure Assisted Membrane Techniques*

Non-pressure assisted membrane techniques like FO and PRO are becoming increasingly relevant in tackling global concerns such as potable water and a secure energy supply. For extracting pure water from the feed side, these techniques need a draw side (DS) that is of osmotic pressure higher than feed water. After that, using a suitable separation method, the product water is extracted from the draw solution. There are various advantages of FO over RO which makes it a viable option for desalination and treatment of wastewater (Jain et al. 2021). FO can solve the fouling problems that plague traditional pressure-based membrane techniques. Since, RO forces all particles from the feed stream onto membrane surface without discrimination, FO enables selective molecules to pass through the membrane by osmotic pressure, reducing fouling and compaction issues. Most importantly, during separation, FO uses almost no external power. To allow fluid circulation in the system, negligible pressure is needed. Poor performance of membranes and inappropriate draw solution that enables for inexpensive and easy recovery are the two biggest obstacles to FO's practical application. Ideal FO membranes shall show high salt rejection, high water flux, and low concentration polarization in general (Su et al.

2012). Moreover, the optimal draw solution should have characteristics like high osmotic potential and cheap cost, as well as the ability to be recovered using simple and cost-effective methods. Ammonium bicarbonate molecular weight is low and has high solubility that is why it was extensively utilized as the draw solution early on in its development. Warming up the chemicals to produce ammonia and carbon dioxide is a simple way to recover it.

Research attempts shifted to using magnetic draw solution generation which allows for easy recovery. Unlike FO methods, which is used for desalting and wastewater remediation, PRO is a new technique that might be utilized for collecting energy by mixing fresh water with saltwater. In theory, PRO is the opposite to RO, except instead of hydraulic pressure, PRO desalinates water while produces energy by using the osmotic pressure of seawater. PRO system utilize the feed solution which is a low concentration side that flows through a membrane into a pressured solution of higher concentration. Power can be generated by depressurizing the permeate with a hydro turbine (Gebreyohannes and Giorno 2016; Klaysom and Vankelecom 2016). The first PRO prototype was commissioned by Statkraft, a Norwegian business, for generating power on the basis of salinity gradient concept using PRO. However, due to the plant's tiny capacity and low osmotic power for practical usage, the unit was shut down a few years later. The most important factor in achieving a commercially appealing power density is a high-performance membrane. In the hybrid RO-PRO system, PRO has also been investigated as a supplementary technique for recycling and reusing RO brine. Instead of being released into the sea, the RO brine concentration can be recycled as a draw solution. Traditional RO membranes were used in PRO procedures throughout the early stages of development. The goal of PRO technology advancement is to create membranes for high-performance.

## 4.3 Membrane Development

### *4.3.1 Membrane Fabrication*

The primary aspect of membrane manufacture is material selection. Polymers and ceramics are the two main materials to consider. The most prevalent type of material utilized to make membranes is polymers (Wen et al. 2019). Polymeric membranes can be made inexpensively thanks to the wide variety of polymeric materials available. The efficiency of many polymer-based membranes is widely examined, and the membrane market has attained maturity. polyetherimide (PEI), Polysulfone (PSf), polyvinylidene fluoride (PVDF), and polyethersulfone (PES) are some of the commercially available polymeric membranes (Jain and Garg 2021). These polymers have a number of desired properties for membrane construction, including simple synthesis, robustness and market availability. Figure 4.1 depicts some fabrication processes for membrane-based treatment of water and wastewater treatment,

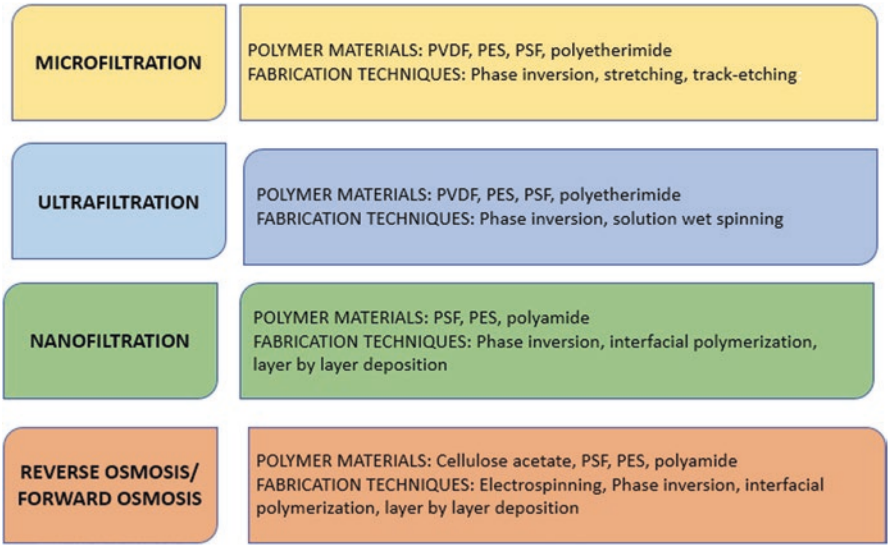

**Fig. 4.1** Membrane processes, materials, and construction techniques for polymeric membranes

as well as the materials and construction techniques that are typically utilized. Ceramic-based membranes have a number of advantages over polymer-based membranes, including good stability as well as mechanical strength. Ceramic membranes can be used in a variety of difficult operating conditions, including a wide range of pH, the use of strong chemicals, and high temperatures (Li et al. 2021). However, when contrasted to their polymeric counterparts, the expense of materials and difficulty in production at larger scale are stumbling blocks that prevent ceramic membranes from being widely used on an industrial scale.

Alumina, zirconia, zeolites, and alumina are some of the commonly used materials for ceramic membranes. Ceramic membranes are predicted to be more feasible in more commercial applications as a result of studies which targets utilizing low-cost substances. Membranes can be constructed in a variety of formats depending on the structural and other operation needs such as throughput and footprint, the two most prevalent of hollow fibre and flat sheet membranes. Because it is simple to perform and because a large range of polymers and solvents are available, phase inversion is a popular method for fabricating membranes. In a nutshell, phase inversion is the separation of polymeric casting solution in a polymeric solid phase (membrane) and a liquid phase by phase shifts (Li et al. 2021; Dong et al. 2021). Surface of membrane is formed by the solid phase, while the liquid phase develops porous structure of the membrane. Surface morphology of the membranes are tailored using nanomaterials to match its application by modifying and optimizing the process' phase transitions. The most difficult aspect of phase inversion is finding a solvent that will thoroughly mix with the polymer and form homogenous blend. Solvents like *N*-Methyl-2-pyrrolidone (NMP), DMAc, and dimethyl sulfoxide (DMS) are routinely utilized to blend polymers including PVDF, PEI, and PSf.

Membrane fabrication via electrospinning is also becoming more prevalent. High voltage is used among a metallic collector and negatively charged polymer solution in this technique (Shiohara et al. 2021). The nozzle release the polymer fibres and these are gathered as a fibrous film with a random orientation. Electrospun fibres have a larger permeability and open porous structure that is interconnected better than a phase inversion membrane. These characteristics are appealing for improving membrane permeability. Commercial uses of electrospinning, on the other hand, are less due to the high cost and difficulty of large-scale production. The membranes utilized in MF, UF, and NF have an asymmetrical structure with a permeable sublayer and an active top selective layer. The bottom layer generally functions as the support layer to offer mechanical strength, while the top layer determines the selective filtration capacity of the membrane (Tibi et al. 2020).

A thin film composite membrane is one that was commonly employed in RO, FO, and PRO processes (TFC). The TFCs are made up of two layers. To generate a polymeric substrate in the UF range, the bottom substrate layer is generally fabricated via phase inversion. Following that, two monomers undergo interfacial polymerization (IP) by dipping the substrate in organic and aqueous solvent to form an active layer, which is usually polyamide. The types and concentrations of monomers, the monomer contact time, the ageing period, and the temperature are all factors to consider during interfacial polymerization (Jain and Garg 2021). These variables can have a significant impact on the density of polymerization, surface shape, and selectivity of the polyamide layer generated. To reduce permeate flow resistance, the thickness of this selective layer is kept to a minimum. Another approach is to cast the polymeric substrate over a layer of polyester fabric to give the TFC membrane more mechanical strength. Layer-by-layer assembly is another appealing way for introducing a selective layer over the substrate. This method is extensively employed in the manufacture of thin films. It works by forming a thick selective layer out of multilayers of oppositely charged polyelectrolytes. Electrostatic attraction between layers is the sole basis for assembly. The layer-by-layer approach has superiority over IP in terms of simplicity and cost. The amount of layers could be adjusted to maximize the selective layer's width, water flux, and selectivity. TFC offers more material design flexibility than asymmetric polymer membranes, as the substrate and active layer can be composed of various materials depending on the solicit qualities for their utilization. Modifications of the membranes can also be carried out individually on the substrate and active layer (Jain et al. 2021).

### *4.3.2 Membrane Modifications*

Membrane changes change the membrane's physicochemical properties, which improve separation performance in terms of flux and rejection. Another goal of membrane modification is to give changed membranes antifouling capabilities (Sadr and Saroj 2015). Fouling is a condition that occurs when chemicals accumulate on the surface or within the membrane structure. Fouling is an unavoidable occurrence which results in a significant drop in its efficiency, notably in terms of membrane flux and productivity (Liu et al. 2019) Fouling also adds to operating costs since it necessitates periodic cleaning of membrane and eventually its replacement. Alterations of membranes can be accomplished in a variety of ways. Polymer mixing can change the surface characteristics of membranes without affecting their bulk shape and properties (Jain et al. 2022). By combining polymers with desirable characteristics and enhancing the flow and selectivity of the resulting membranes, blending different polymers can drastically alter the hydrophilic-hydrophobic balance of the membrane. Physical and chemical approaches of membrane surface modification can be broadly classified. The altering substances are glazed on the surface of membrane in the first technique, which does not require the creation of covalent bonds (Seo et al. 2018).

As a result, the membranes' chemical characteristics are largely preserved after alteration. Dip-coating hydrophilic components like chitosan and polyethylene glycol onto the membrane surface can improve the membrane's hydrophilicity. Direct pressure sieving of hydrophilic substances over the membrane surface can be used to coat the surface. Physical interactions, such as electrostatic attraction, keep the coated or adsorbed compounds on the membrane surface. As a result, the coated components' poor adherence to the membrane surface is a shortcoming of this modification process. After a specific length of operation, the glazed substances separate from the surface smoothly. To address this issue, several attempts are made for functional groups introduction which acts like bridging agents and anchor sites, allowing chemical bonding among the glazed substances and surface of membrane to be established (Homaeigohar and Elbahri 2017). Covalent bonds are produced in chemical modification by interlinkage among agents and surface. Before reactions with foreign chemicals, the surface is frequently activated by irradiation chemically. Chemical alteration, as opposed to physical techniques, can provide more stability so the transformed surface would be intact for extended periods of time The use of plasma to produce active groups on the membrane surface is a straightforward modification procedure. The production of oxidative groups on the surface can be aided by inert gases like helium (He) and argon (Ar). The increased flux can thus be attributed to hydroperoxides and peroxides. The key issue with this technology is maintaining membrane integrity, as plasma treatment includes a complicated reaction that might destroy the membrane structure, resulting in a loss of mechanical strength. A diverse strategy to changing polymeric membranes is grafting, which involves activation of the surface utilizing processes such as polymerization, UV photoirradiation, and plasma.

Owing to its simpleness, power economy, and cost-effectiveness, UV photon irradiation is the most extensively used of these activation approaches (Oulad et al. 2021). It can be done on flat sheet and hollow fibre membranes both with UV irradiation generating surface radicals that serve as monomer anchor sites. Advances in nano science has paved the way for more novel membrane designs. The manufacturing of high-performance membranes has been made possible because to the intriguing features of diverse kinds of nanomaterials. The hydrophilic metal-oxide nanomaterials, the hollow structured nanocomposites, and the antimicrobial metal nanomaterials are used to increase the flux, rejection, and antifouling properties of membranes. Nanoparticles and membrane materials have been combined to generate nanocomposite or mixed matrix membranes, which aim to translate the unique features of nanomaterials to membranes (Giwa et al. 2016).

When metal oxides like $TiO_2$ and $Fe_2O_3$ are added to nanocomposite membranes, their hydrophilicity improves dramatically, increasing membrane flow and consequently separation productivity (Guan et al. 2019). Carbon nanotubes (CNTs) and titania nanotubes (TNTs) are employed successfully in these applications. The tubular structure of CNT helps in rapid and low-resistance passage of water molecules across the hollows. Hence, the water flux of the membrane can be increased by several orders of magnitude. Enhanced hydrophilicity of membrane also helps with antifouling qualities. The ability of nonpolar substances like proteins and organics to get attached can be lessened with increased hydrophilicity. Nanoparticles with antimicrobial properties such as silver-based nanomaterials and single-walled carbon nanotubes (SWCNTs) play a significant role in prevention of biofouling. Membrane adherence by algae, fungi, and bacteria exerts a substantial negative influence on the membranes. Biofouling, unlike the previously described inorganic and organic fouling can be a concern since the microbes have ability to replicate over time and cannot be properly dealt with standard cleaning (Adamczak et al. 2019). Silver nanoparticles' antibacterial capabilities help regulate and decrease fouling by preventing growth of biofilm on the surface. Several methods for introducing nanoparticles into the polymer matrix have been developed. One of the most often described methods is the direct incorporation of nanoparticles into the polymer casting solution prior to membrane casting or spinning. Grafting and coating nanoparticles onto the produced membranes is another widely used method. The nanoparticles are deposited onto the membrane surface as a result of the physical and chemical interaction, which provides the maximal nanoparticles exposure (Gann and Yan 2008).

Such strategies are especially appealing for nanomaterials with antibacterial characteristics. The direct interlinkage of silver-based nanomaterials grafted or coated on the surface of the membrane via wastewater having bacteria or fungus like Staphylococcus aureus and E. coli can optimize silver-based nanoparticles' growth inhibitory effects. Mechanical strength is a critical consideration, especially for extended high-pressure operations like RO and nanofiltration. The membrane's great mechanical strength allows it to keep its integrity, also, withstand collapse and structure change produced by high-pressure compaction. As reinforcing materials, carbon-based nanomaterials like multi-walled carbon nanotubes and oxide of graphene have been used. The incorporation of these nanoparticles into the polymer matrix improves mechanical strength by allowing load transfer between the two entities (Jiang et al. 2020). Despite the intriguing capabilities given by these nanoparticles in enhancing the characteristics of the nanoparticle loaded membrane, the dispersion condition of the nanomaterials within the polymers is the most important factor in successful membrane modification utilising nanomaterials. Because of their large surface area, nanomaterials tend to clump together (Kim et al. 2018). The creation of gaps at the polymer and nanomaterial interface occurs as a result of aggregation inside the matrix, reducing the nanomaterials' distinctive characteristics. Because of the creation of unwanted voids, the agglomeration of nanoparticles placed inside the active layer of thin-film nanocomposite (TFNC) membrane resulting in significant decline rejection efficiency. Various types of nanomaterial alteration have been researched to address this issue. Some frequent nanomaterial changes include silanization, molecular wrapping, mild acid oxidation, and surfactant dispersion (Ihsanullah 2019). Commonly, these changes can add surface functions to nanoparticles in order to improve the compatibility of modified nanomaterials with the polymer matrix and achieve greater dispersion. Another appealing concept for membrane alteration is the creation of a biomimetic membrane, which incorporates biological features such as aquaporin to mimic biological processes (Li et al. 2017). A membrane like this is stimulated by natural efficiency and selectivity transport which developed over billions of years in live creatures. The UF and RO-FO membranes are related by the exterior surface membrane layer having pore range of 2–8 nm and lipid nanoporous bilayer. The protein-facilitated lipid bilayer is employed like a channel to increase flow of the biomimetic membranes by facilitating water transport. The biological antifouling surface, which can be employed to treat biofoulants (tiny proteins or complete organisms) is an intriguing property that can be used to give biomimetic membranes antibiofouling properties. Surface physiochemical interactions that resist foulants, release compounds that hinder biofilm adhesion, and other mechanisms are all involved in antifouling and build a topology which can minimize interaction among the surface of membrane and the biological surface (Shen et al. 2014).

### *4.3.3 Innovative Membranes*

Adding capabilities and extra roles to membranes is another excellent technique to improve the performance of membrane technology. Photocatalytic and adsorptive membranes are two relatively novel kinds of membranes obtained from traditional MF-UF techniques (Nascimbén Santos et al. 2020). Because of the unique properties of the materials, adsorption and photocatalysis are utilized for the treatment of wastewater. When exposed to UV or visible light, photocatalysts degrade undesirable organic contaminants through a photodegradation reaction. Adsorbents eliminate pollutants from the environment either by physical or chemical reactions between adsorbent and pollutants surfaces. In spite of efficiency of these procedures, the handling strain of photocatalysts and adsorbents after water treatment limits their practical utility. For separating particles from the aqueous media, further treatment is always required. Photocatalytic and adsorptive membrane innovations have helped to solve these problems. Adsorbents and photocatalysts are inserted inside matrix of membrane that acts as a host for such components in these membranes. Before being inserted into the polymeric membrane matrix, the photocatalyst and adsorbent materials are typically produced or adjusted for optimal performance efficiency. Synergistic effects can be accomplished by innovative membrane design so that membrane can undergo adsorption and photocatalysis and separating undesirable molecules (Zhang et al. 2021). Because the photocatalyst and adsorbent materials are incorporated into the membrane matrix, it can be re-utilized and the secondary particle separation process could get eliminated.

## 4.4 Membrane-Based Remediation of Wastewater

### *4.4.1 Removal of Heavy Metal Ions*

The heavy metal ions like chromium (Cr), arsenic (As), and lead (Pb) have wreaked havoc on the environment and harmed people's health. Due to the surface charge and sieving effects of such ions, reverse osmosis and nanofiltration may efficiently eliminate heavy metal ions from water and wastewater (Qasem et al. 2021). However, due to the low productivity and higher consumption of power, attempts are made to increase the selectivity of traditional UF and MF membranes toward heavy metal ions. Utilizing cellulose acetate (CA) based UF membranes infused with titanium dioxide ($TiO_2$) nanomaterial, Gebru and Das (2018) were able to remove chromium (VI) ions. The titanium particles were treated with amine ($–NH_2$) functional groups to produce chemical interactions among metal ion and the amine groups, which improved the affinity of heavy metal ions toward the membrane and improved reduction efficiency. Because of the porous nature and high surface area of $TiO_2$ nanoparticles, aminations were easily carried out within the pores. Figure 4.2 shows different adsorptive membranes (AMs) in the removal of heavy metal (Vo et al. 2020).

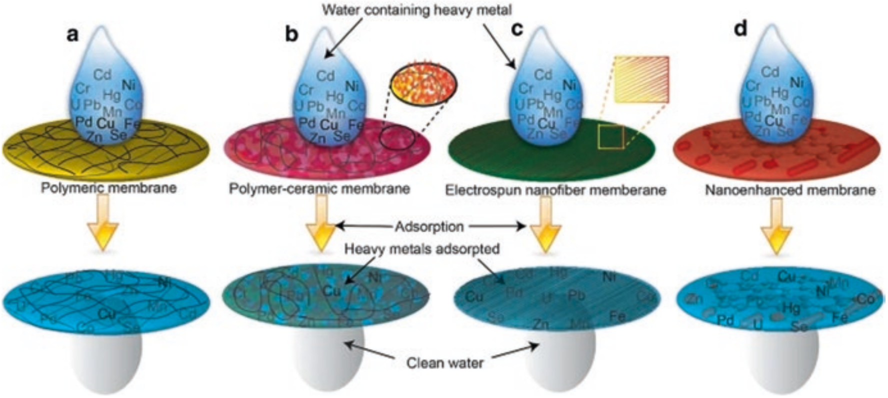

**Fig. 4.2** Different adsorptive membranes (AMs) in the removal of heavy metal. (**a**) Polymeric membranes (PMs) are created from polymer (Vo et al. 2020). Source materials, (**b**) polymer-ceramic membranes (PCMs) are created from a combination between polymeric and ceramic (natural clay materials: bentonite, kaolinite, and montmorillonite) materials, (**c**) electrospinning nanofiber membranes (ENMs) are created from electrospinning method for forming fibers with nanometer to micron diameters, and (**d**) nano-enhanced membranes (NEMs) are created from incorporating nanomaterials (carbonaceous materilas, nanometal or nanometal oxides, and other organics)

At pH 3.5, the inclusion of $TiO_2$ nanomaterials enhanced reduction efficacy, resulting in 99.7% Cr (VI) removal. The protonated $–NH_2$ bonds in $TiO_2$ nanomaterials developed electrostatic contact with Cr (VI) anions like chromate (VI) ions at this pH. Addition of $TiO_2$ nanomaterials increased membranes' antifouling capabilities, making them easier to clean and regenerate. After regeneration and washing cycles, the reduction efficacy was only slightly reduced to 96.5%. Modified ultrafiltration membranes for the elimination of heavy metal ions was also reported by Fang et al. (2017). Adsorptive UV membranes were generated in their research by self-polymerizing polydopamine nanoparticles into the membrane's interior holes. Through circulatory filtration, a three-dimensional network of polydopamine was generated within the porous structure of the PES membrane from bottom to top. The inclusion of these nanomaterials increased the number of active sites and increased the contact time for heavy metal ion adsorption on the membranes. As a consequence, $Pb^2$, $Cu^2$, and $Cd^2$ adsorption capacities on PES-PDA-R membranes were 20.23, 10.42, and 17.01 mg/g, respectively.

However, regeneration investigations revealed that the increased polydopamine was not washable. As a result, only roughly 84.6% of the performance was recovered. The FO process is considered promising low-energy based method for the removal of heavy metal ions. To produce a polymer network, Liu et al. used a layer-by-layer technique to create a FO membrane. By using a polydopamine functionalized PVDF substrate, polyethylenimine (PEI), and sodium alginate were alternately constructed. Various heavy metal ions, including (Liu et al. 2017) $Cu^2$, $Ni^2$, $Pb^2$, $Zn^2$, and $Cd^2$, were removed from the aqueous solution using the resulting FO membranes. The bilayers amount in the membrane, the feed and draw solutions concentration, wastewater pH, time, and temperature were all investigated and compared. When three bilayers on the PVDF substrate with 1 molar magnesium chloride (MgCl) was employed on the draw side, an optimum 99% heavy metal reduction for all heavy metal was attained. The FO membrane's great rejection was due to optimal bilayers quantity that had produced an appropriate compactness and thickness to prevent heavy metal ions from passing through without impairing flow. The maximum rejection of 99.3% resulted in a flow of 14 $L/m^2$ h.

### 4.4.2 *Removal of Colour*

Large-scale discharges of colour through pigments and dyes in the water bodies are major source of worry since they possess immediate health and environmental risks. In this regard, ultrafiltration hollow fibre photocatalytic membranes with varied TNT weight fractions were produced by Subramaniam et al. (2018). TNT, which is a tubular shaped $TiO_2$ nanostructure which has been widely employed to enhance the hydrophilicity of the nanocomposite membranes. TNT has a large surface area functionalized with surface hydroxyl groups due to its tubular structure which provides more number of surface active sites for the attachment of functional groups. The PVDF-TNT membranes were utilized in that investigation to treat effluent of palm oil mill (AT-POME), that showed a brownish colour appearance. The fabricated PVDF membranes that had 0.5 weight fraction TNT amount gave the best filtering with 59.4% colour removal and a flux of 35.7 L/m$^2$ h. The increased flux was attributed by increased membrane hydrophilicity produced due to abundant hydroxyl groups observed at the TNT surface, as compared to the plain PVDF membrane. These hydroxyl groups made it easier for water to pass through the membranes. All the nanocomposite titania membranes had low fouling and maintained recovery flux of 80% after five cycles of operation, according to the membrane fouling and reusability analyses. The performance of that membrane photocatalytic membrane reactor under UV light irradiation was reported by the same group of researchers. TNT's photocatalytic property was activated by UV light, allowing for simultaneous filtering and photodegradation. When the photocatalytic property was activated, the colour removal effectiveness increased dramatically from 34 to 67% when compared to filtration alone. TNT served as a photocatalyst for lignin and tannin pigments to degrade in the AT-POME effluent in this environment, as well as an addition to increase the membranes' hydrophilicity. In addition, as the foulants photodegraded into smaller compounds, the photocatalytic activity showed positive effect by decreasing the fouling susceptibility. After five cycles of operation, the flux loss was only 5.7%.

PVDF NF membranes with halloysite nanotubes (HNT) were manufactured by Zeng et al. (2016). To combat HNT aggregation, the layered nanomaterials were treated by a coupling agent using a 3-aminopropyltriethoxy-silane silane to promote dispersion prior being added to the polymer dope. The ability of the resulting membrane to remove Direct Red 28 dye was tested. The inclusion of HNT enhanced the membranes' hydrophilicity, allowing for easier water transport while preventing dye molecules from passing through. Due to negative charges of HNT nanocomposite, an electrostatic connection between dye and membrane was generated, which enabled dye rejection. The developed membrane with 3 weight fraction silanated HNT achieved the greatest rejection of 95%. Chen et al. created a biomimetic dynamic membrane for dye wastewater treatment in another investigation (Chen et al. 2019).

Physical adsorption and filtration were used to introduce laccases and carbon nanotubes to the surface of a commercial UF membrane. CNTs worked as an absorbent in this nanocomposite system, preventing dye molecules from making contact with the surface of membrane. Laccase enzyme which was embedded inside absorptive layer boosted enzyme activity and aided pollutant breakdown in real time. Adsorption and fouling of membrane could thus be reduced at the same time. On dye removal, the effects of adsorbents and enzymes were investigated. A sustainable capacity was achieved at comparative high amount of laccase at 74.5 g/m$^2$ and the enzyme could successfully execute catalytic degradation to limit the propensity of absorption saturation. Furthermore, to obtain optimal dye removal efficiency, just 19 g/m$^2$ of CNT was required. The biomimetic dynamic membrane displayed greater antifouling performance and extended reusability due to the synergistic actions of the absorbent and enzyme. Moreover, after various cycles of operation, the flux remained over 120 L/m$^2$ h. The foulants might also be easily eliminated after the absorption process with a simple backwash cleaning.

### 4.4.3 Treatment of Oily Wastewater

Membranes in oily wastewater or generated water treatment tend to foul readily due to their nature (Barambu et al. 2021). As a result, it is preferable to build highly antifouling membranes for this application to ensure their long-term viability. Zwitterionic polymers are evolving as modifying agents which gives modified membranes antifouling capabilities. They possess equal number of anionic and cationic groups in their molecular chain, giving them hydrophilicity and resistance to nonspecific protein adsorption and bacterial adhesion. Zwitterionic substances surface grafting on UF and FO membranes has been widely used to treat oily wastewater. A double-skinned FO membrane was created by Ong et al., consisting of a PES substrate sandwiched between a selective polyamide top layer and a zwitterionic brush at the bottom layer. The hydrophilicity of PES was improved by grafting a poly(3-(*N*-2-methacryloyloxyethyl-*N*,*N*-dimethyl)ammonatopropanesulfonate) (PMAPS) brush to the bottom surface. The double-skinned membrane had a high water flux of 13.6 L/m$^2$ h and a reverse salt flux of 1.5 g/m$^2$ h when evaluated in a FO mode with 2 M NaCl as the draw solution, with a rejection of 99.8%. Lee et al. devised a more straightforward method of inserting the PMAP zwitterionic polymer onto the PES substrate of a FO TFC membrane. The hydrophilic nature of PMAPSs permitted the creation of finger-like structures on the PES substrate during phase inversion, that facilitated transport of water molecules. Moreover, 99.9% of oil rejection and flux of 15.7 L/m$^2$ h was observed when TFC was combined with 1 wt% PMAPs. When compared to the unaltered TFC, the flow was increased by over 30%. The membrane displayed good water recovery even after possessing very high oil emulsion concentration of 10,000 parts per million (ppm) due to its significant hydrophilicity. To recover the flow, only deionized water rinse was necessary. The hydration layer generated by hydroxyl bonding between the feed water and –SO$_3$ functional groups of PMAPS that prevented oil molecules from attaching to the membrane and increased its antifouling characteristics. Figure 4.3 shows the modified and unmodified membrane fouling mechanism.

Yan et al. (2008) used the intercepting outcome of a permeable CNT framework to create a hybrid membrane. Through covalent functionalization, polyacrylic (PAC) acid brushes that were hydrophilic in nature were introduced into the CNTs structure to generate a underwater superoleophobic structure. The membrane porosity was proportionate to its thickness and the functionalization was done using a simple filtration process. The superoleophobic surface of membrane facilitated quick water movement while obtaining a separation efficiency of 99% while filtration of the oily water under vacuum pressure of 0.09 MPa.

Ahmadi et al. (2017) created antifouling nanofibrous MF membranes incorporating GO. Electrospinning was used to create the membrane, which was made up of sulfonated PVDF, PVDF, and GO. Membrane hydrophilicity was enhanced at an optimal 0.5 wt% of GO due to existence of several hydrophilic groups on the GO planar structure. The membrane was able to completely remove the oil due to membrane smaller pore size, which successfully blocked oil particles transfer through the membranes. The antifouling properties were increased by repulsion among oil particles and sulfonic groups. Nanofibrous membrane showed less irreversible fouling (41%) with good recovery ratio (59%). For treating generated water, Ahmad et al. (2018) modified flat sheet polyvinyl chloride (PVC) UF membranes via incorporating bentonite particles to enhance morphology and antifouling characteristics. Bentonite particles having good cation exchange capacity played key role in modifying the viscosity of dope solution, as well as the morphology of the membranes. The introduction of bentonite nanoparticles increased viscosity of the gelation bath, which enhanced the exchange rate of water and solvent. The UF-PVC membrane with the largest loss tangent and dynamic viscosity had a polymer, solvent, and nanocomposite at a ratio of 12.0:87.23:0.77. As a result, the surface porosity, density, and roughness were significantly improved. On treating with oily water, the UF nanocomposite membrane had a 97% oil rejection and a flux of 186 L/m$^2$/h with the necessary morphological features. When operated with generated water with TDS of 35,000 ppm, the membrane achieved 93% oil rejection and 94 L/m$^2$ h water flux thanks to bentonite's strong hydrophilicity and antifouling capabilities.

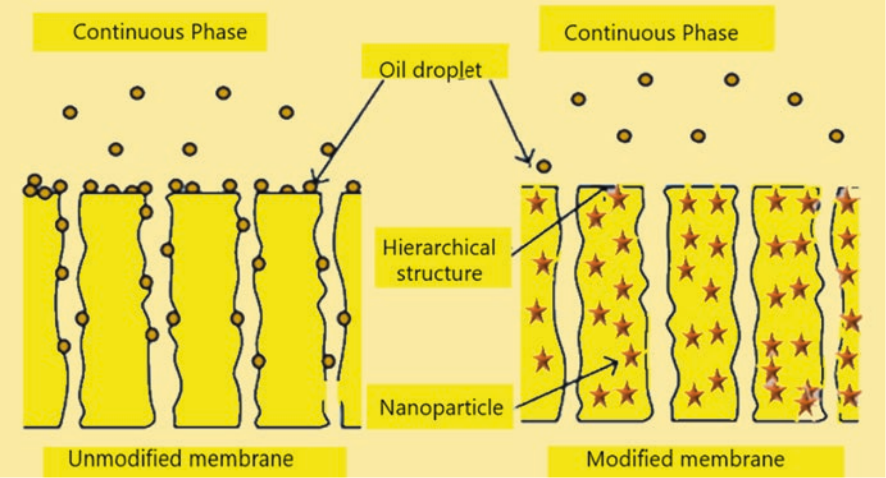

**Fig. 4.3** Illustration of fouling mechanism of nanocomposite membranes

## 4.5 Innovative and Sustainable Membrane Techniques

Membrane-based processes plays a critical role in preserving water supplies from a variety of water sources, including wastewater and seawater. The long-term viability of membrane development is largely responsible for their growing acceptance and application in industries (Tufa 2015). Membrane technologies have a number of advantages over traditional techniques, which has spurred the move. Membrane process allows for localized reclamation and reusage, as well as the avoidance of long-distance product water transfers. It is also unnecessary to identify new protected catchments. Membrane techniques have also demonstrated promising factors in terms of technical factors including durability, easy handling, scalability, flexibility and adaptation. Different membrane techniques for desalination and the treatment of wastewater production have been evaluated with various economic, ecological, technological, and societal implications to assure the long-term development of membrane technology. The cost of desalination and the treatment of wastewater, as well as the environment impacts of these techniques are major drivers for membrane development's long-term viability (Goh et al. 2020). The biggest impedance in terms of economics is energy consumption, particularly in the case of RO saltwater desalination. To create 1 $m^3$ of freshwater, modern RO plants typically consume 3–4 kWh of electricity. The pressurization of seawater to 60–70 bars consumes a significant amount of energy. Another major concern with pressure-based membrane techniques is the release of greenhouse gases (GHGs) and other pollutants into the atmosphere, that may accelerate climate change. Alternative resources, such as renewables, are one long-term answer to this problem.

The ideology of employing renewable resources is appealing, and the number of studies is growing as a result of the enormous potential of renewable resource-driven RO desalination plants to meet water demand while lowering $CO_2$ emissions. Solar, geothermal, and wind energy have all been examined as potential sources of power for desalination plants. However, various technological restrictions linked to resource stability and building expense must be overcome before large-scale applications can be implemented (Eggensperger et al. 2020). To justify ethical difficulties linked with membrane implementation, it is vital to identify probable environmental dangers involved in membrane manufacture and during the procedures. Direct and indirect environmental effects are two types of potential environmental consequences. In the case of desalination, the direct effect is caused by the intake of saltwater, that results in a significant reduction of aquatic species when brought near desalination plant. If the discharge is not effectively handled, membrane processes can pose a harm to the environment, particularly to marine organisms. The brine discharge with high total dissolved solid (TDS) contents from RO plants, in particular, has considerable negative environmental consequences. The Ashkelon desalination plant, which has a monthly seawater input of roughly 315 million $m^3$ and releases brine with a TDS about double that of seawater, has been confirmed to be one of the world's largest facilities. Material selection, regulatory enforcement strategies, and process intensification can have a significant role on minimizing the global environmental concern. Membrane fabrication development and utilization is expanding. The incorporation of nanoparticles as additives in membrane production offers a significant performance boost (Fane and Fane 2005).

As previously noted, several developments in studies have seen the promise of reducing membrane process energy consumption by inventing revolutionary nanocomposite membranes that can efficiently boost the flow and supply of fresh water. In spite of their benefits, nanoparticles' environmental friendliness, stability, and applicability in improving membrane techniques are still contested. To synthesize nanomaterials, various hierarchical techniques have been well-entrenched. Some of these methods, however, necessitate elevated temperatures and the toxic chemicals usage. The green synthesis of nanoparticles, which can limit the creation of toxic by-products to the ecosystem, is an essential area for concentration in this subject to ensure sustainable development. Furthermore, the leaching of nanoparticles from nanocomposite membranes could be hazardous to the environment. Coating and grafting are two nanocomposite membrane production procedures that include the deposition or attachment of nanoparticles on the membrane surface. The durability and stability of the membrane might get impaired in the coarse of extended operations and high pressure conditions, resulting in nanomaterial leakage into water bodies. Hence, long-term performance review is essential to avoid secondary contamination. Nanomaterials' unique features, as well as the nanocomposite membranes that result, have allowed for extraordinary improvements in membrane performance (Buonomenna 2013).

Production of nanoparticles on larger scale to fulfil industrial necessities, on the other hand, is a huge obstacle that must be overcome. Many nanomaterial synthesis processes necessitate meticulously controlled reaction conditions in order to achieve a low yield of nanoparticles with desirable characteristics. To accelerate the use of this invention in industry, easy, reliable, and repeatable synthesis procedures are required. The long-term reliability of membrane techniques is critical for the technology's long-term development. Membrane fouling is a key source of worry, since it has resulted in a drop in performance. The impact of membrane fouling on flow and productivity has been thoroughly examined using the concept of critical water flux. Cleaning of membrane is done on a regular basis to eliminate fouling layers before membrane replacement. Various cleaning regimens have been thoroughly investigated; the most simple and successful cleaning processes uses the treatment with chemicals. Chlorine bleach, sodium hydroxide (NaOH), and hydrochloric acid (HCL) are some chemicals used in the chemical cleaning process to eliminate the foulant before the conventional backward or forward flushing. Though, the brine discharge did not pose substantial toxicity on the examined aquatic creatures, Park et al. (2011) found considerable toxicity in the additives, chemicals and solvents utilized for cleaning of membrane in a case study based on the desalination facility at Chuja Island, Korea. To reduce negative consequences of chemical discharge, ecofriendly chemicals must be chosen and low concentrations must be used.

## 4.6 Conclusion

Membrane technology for desalination and wastewater treatment has shown continuous and continual improvement. Membrane-based processes are becoming popular replacement to several commonly utilized procedures due to its benefits. The membranes structural design to improve filtration efficiency is one of the most significant areas of advancement in this industry. The choice of an appropriate membrane technique and the membrane parameters optimization for the specific application criteria are critical since they determine the effectiveness of salt and impurities removal capability as well as the cost of the technique. This chapter focuses on developing high-performance membranes for a variety of applications, including heavy metal ions and colour removal, treatment of oily wastewater and desalination. Various manufacturing processes for membrane modification have been devised and effectively used to increase membrane separation performance and long-term stability. The affinity of membrane materials with additives, the durability and stability of membrane fabrication materials for modifications that may imply extreme conditions, economic efficiency, separation purpose, operation types and feasibility for large-scale operations, all play a role in the selection of an appropriate method. High-performance membrane process is expected to evolve in different filtration technologies, feasibility on a large commercial scale, as improvements in membrane development and system optimization are made. Moreover, despite membrane technologies' potential in solving numerous challenges connected to desalination and treatment of water and wastewater, their adoption should be constantly studied in order to assess its extended time period impacts, especially from an ecological and environmental standpoint.

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# Chapter 5
# Recent Advancement and Efficiency Hindering Factors in the Wastewater Treatment Plant: A Review

**Mamta Awasthi and Tushar Moten**

**Abstract** Industrial discharge and toxic waste through domestic dwellers with changing lifestyle have increased. Wastewater treatment plants must cope up with the increasing quantity and toxicity with various treatment units. Modifications in the treatment units can enhance the treatment process. The review emphasizes on the state of the art of the wastewater treatment system. The article emphasizes on the economic and effective alternative method and discusses the recent advancements in the field in each step of the treatment processes. Recent research work on techniques to recover the nutrients and other value-added products has been discussed. Various modeling tools are talked about that could be used for maintaining and operating the treatment units, e.g., Fuzzy-based Module (for wastewater discharge from the equalization tank), Artificial Neural Network (ANN) to predict total and fecal coliform removal or TOXCHEM for fate and emission of $H_2S$. Some research workers laid emphasis on large-scale hydrogen recovery and production of biodiesel from Waste Activated Sludge (WAS). Different medias such as sponge bed, bamboo chips, maize cobs, sugarcane bagasse, etc. are suggested for trickling filter instead of rocks and gravel. The study will help to summarize the latest research areas in the field and identify the gaps for further advancement.

**Keywords** Wastewater treatment · Modeling tools · Pulp and paper industry in India · Primary filtration · Conventional Primary Clarification methods · Industrial discharge and toxic waste · Equalization tank · Total and fecal coliform removal

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## 5.1 Introduction

Improper disposal of wastewater has severe impact on the surroundings and one of the most direct environmental impacts is the degradation of aquatic life, soil deterioration, which results in decreased crop yields and heavy metal ions found in polluted water are usually absorbed by the plants, enters the food chains and causing severe humans and wildlife health effects. Since these heavy metal ions are not really absorbed by the body, they accumulate in soft tissues, posing a health risk. According to the United Nations, 80% of worldwide wastewater is dumped into the environment, sometimes without any treatment and sometimes with a little treatment. With the increase in population and large-scale change in human lifestyle, a lot of eco-environmental issues regarding the water resource utilization have occurred. The majority of heavy metal contents continue to exceed the specified standards. Furthermore, the growing need for clean water in growing cities, for sustainable farming, and to boost energy output in industrial growth necessitates the use of high-quality treated wastewater. However, the challenges of reusing the treated wastewater remain high (Meese et al. 2021).

The primary goal of wastewater treatment is to enable industrial and human greywater to be discharged in a safe and environmentally friendly manner. Since industrial discharge from factories and increasingly toxic waste by domestic dwellers has increased, wastewater treatment plants must comply with the volumes and contamination. The wastewater is treated and utilized for different purposes through technological advances in different treatment units to be discarded safely while minimizing environmental and health risks (Mandal et al. 2020; Abinandan et al. 2018).

If water contamination has been found and unsafe levels of toxins remain, remedial techniques must be selected and implemented (Tang et al. 2021). In recent years, nanoscale zero-valent iron (NZVI), with diameters of the nanoscale range (1–100 nm) and it is an environmentally friendly material with high reactivity, strong treated efficiency, controllable particle size, and abundant activate sites, has become a promising material for removing common contaminants from aqueous solutions. Bioelectrochemical systems (BESs) are versatile electrochemical technologies that use microbial catalysts for simultaneously harvesting energy and treating wastewater. Membrane-based technologies for water/wastewater treatment and energy production, such as electrodialysis, forward osmosis, reverse electrodialysis, and pressurized filtration (e.g., ultrafiltration), have been integrated into BESs (Yang et al. 2019). The integration of membrane system with BESs has created new systems including microbial desalination cells, osmotic microbial fuel cells, pressurized filtration-microbial fuel cells, and microbial reverse electrodialysis cells. Wastewater treatment technologies were first created in response to the negative effects that waste water has on the environment. There is a great need of designing a cost-efficient wastewater treatment facility. For this, the treatment facilities are equipped with novel techniques that not only require precision but also sufficient funds for the set up. Water contamination management options include chemical, physical, and biological treatments. Digestion, filtration, membrane filtering, and other processes are among them. For efficient water pollution restoration, most treatment methods are utilized in combination with other treatment techniques. For instance, when treating industrial waste water, the initial step is the removal of solid matter from the wastewater, followed by adsorption, sedimentation, bioremediation, and other techniques. Advances in adsorption of contaminants through conventional and green material are also reported (Saleh 2021; Lim et al. 2018). Semiconductor photothermal materials are also currently used for desalination and treatment of wastewater (Ibrahim et al. 2021). Several classes of rationally-designed photothermal materials (PTMs) and nanostructures have enabled effective absorption of broad solar spectrum resulting in improved solar evaporation efficiency for sludge treatment and desalinization. Modeling and simulation tools are the most reliable techniques to achieve the demand. The goal is to achieve chemical and microbiological quality standards at a minimal price and with limited maintenance and operational demands. An efficient way of wastewater exploitation is by using it for irrigational works and thus the wastewater can be both utilized and disposed. Wastewater contains certain harmful constituents that must be removed, these constituents may be, colloidal particles, floatable substances, suspended particles, organic matter, pathogens, phosphorus and nitrogen, heavy metals, and certain energy rich substances. Ahmed et al. (2021) discussed the use of algal biomass for the removal of contaminants from wastewater. Other biological techniques are also reported for specific wastewater for resource recovery (Cheng et al. 2020). Various methods like incineration, pyrolysis, anaerobic digestion, gasification is used to produce biofuel and bioelectricity by providing certain modifications in the current municipal and industrial wastewater treatment process and various waste-to-energy technologies are developing for converting municipal solid wastes into a variety of useful products such as electricity, liquid fuels, fertilizers, and chemicals (Vaish et al. 2019). Efforts are being made for the generation of clean Sludge and the extraction of energy rich compounds. Also, different nutrient removal processes are being used to reclaim phosphorus, nitrogen, and other minerals (Bunce et al. 2018). Some recent advances for the recovery of nutrients from wastewater are also reported (Jafarinejad 2021). Microbial Fuel Cell (MFC) technology is an alternative for energy positive wastewater treatment and permits synchronized wastewater treatment, bioelectricity production, and resource recovery via bioelectrochemical remediation mediated by electroactive microbes. MFCs can both substitute and complement the conventional energy-intensive technologies for efficient removal as well as the recovery of sulfate, nitrogen, and phosphate without any tertiary treatment (Kumar et al. 2019a, b).

A lot of recent developments in the current treatment system, introduction and modification in treatment units, and modeling tools for better treatment of the effluent are in progress and much more is in demand. This article discusses the treatment process to reflect the advancement and evolution of the wastewater treatment plant treatment units and the factors that may affect the wastewater treatment efficiency. Research work pursued mostly in the last decade has been sorted and reviewed.

## 5.2 Methodology

After an immense search for articles in the Science Direct, Web of Science, and Google Scholar databases, a decent number of articles were identified for writing the review. Around 1005 articles were found with the keyword, “recent wastewater techniques,” “advancement in wastewater,” “Nutrient removal wastewater,” “heavy metal removal wastewater,” “agriculture use wastewater,” “wastewater treatment” or “primary Clarifier” or “Secondary Clarifier” or “Tertiary Treatment.” Further refining of the research articles with keywords “Grit Removal” or “Equalizing Tank” or “modeling” or “Activated Sludge (AS)”or “Moving Bed Biofilm Reactor (MBBR)”or “Trickling Filter (TF)”or “Extended Aeration (EA)”or “Waste Activated Sludge (WAS)”from 2010 to 2021, gave a total of 115 articles. Due to lack of information, some research articles had to be selected from the years before 2010. After this, each of the papers was manually screened, based on the content that focused on the recent advancement in wastewater treatment and the factors that may affect the treatment efficiency, by going through the abstract, results, and conclusion of each article. Out of these 115 articles, around 82 articles were finalized that contained all the necessary information for this review article. Some of the articles were then categorized according to their use in the treatment unit. For example, articles focusing on equalizing tanks were kept under preliminary treatment. Figure 5.1 shows the flow chart of the research work.

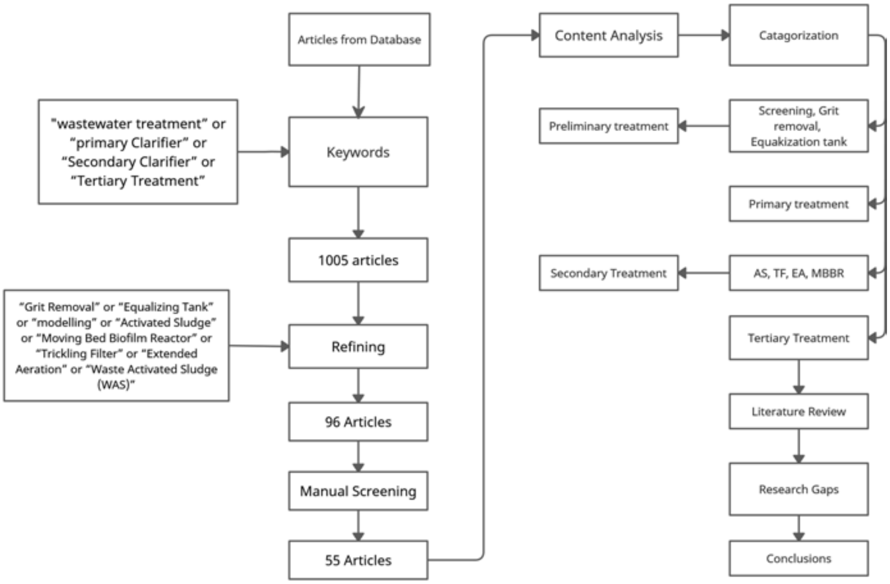

**Fig. 5.1** Flow chart of the research

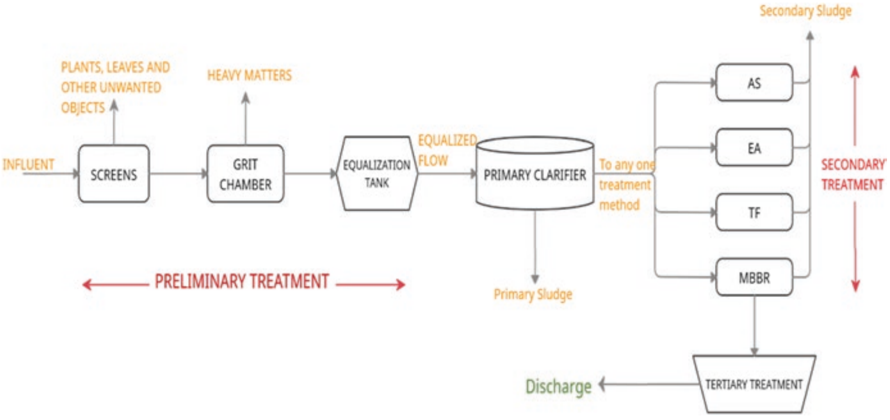

**Fig. 5.2** Flow chart of the wastewater treatment process

## 5.3 State of the Art in the Wastewater Treatment Processes

The treatment unit is categorized as preliminary, primary, secondary, and tertiary and all the advancements in the field are given in each category. The categorization was done after a thorough content analysis of the research articles. The articles are sorted according to their focused treatment unit. Figure 5.2 depicts the treatment process along with the category. Several modeling tools could be used in a treatment unit. The modeling tools and methods are categorized and discussed based on their use in a specific wastewater treatment unit. Some modeling tools can be used in any of the treatment units or can be used for full-time monitoring of wastewater treatment. Semi-supervised soft sensors, BNRM (Biological Nutrient Removal Model), classical On/Off control algorithms, software BioWin are some of the examples of the modeling tools and methods for the whole treatment process (Table 5.1).

### *5.3.1 Preliminary Treatment*

The purpose of preliminary treatment is the removal of bigger and coarse objects that may be present in raw wastewater and to make the wastewater consistent for the treatment.

#### 5.3.1.1 Screening

These contain bars that are placed vertically and horizontally to remove the coarse objects from the raw wastewater. These devices eliminate coarse material (such as sediments, rags, and sticks), which can obstruct downstream pipes and ducts and

**Table 5.1** Methods and modeling tools applied for the wastewater treatment units

| S. No | Title | Method | Author | Treatment unit in which the tool is applied |
|---|---|---|---|---|
| 1. | Continuous versus single $H_2O_2$ addition in peroxone process: Performance improvement and modeling in wastewater effluents | Based on $R_{OHO3}$ and $UVA_{254}$ measurements. | Cruz-Alcalde et al. (2020) | Tertiary treatment |
| 2. | A novel two-step adaptive multioutput semi-supervised soft sensor with applications in wastewater treatment | Semi-supervised soft sensor | Li et al. (2021) | In any unit |
| 3. | Plant-wide modeling in wastewater treatment: Showcasing experiences using the biological nutrient removal model | BNRM (biological nutrient removal model) | Seco et al. (2020) | In any unit |
| 4. | Monitoring and modeling of influent patterns, phase distribution and removal of 20 elements in two primary wastewater treatment plants in Norway | Influent generator model and multivariate statistical analyses | Farkas et al. (2020) | Primary treatment |
| 5. | A design of higher-level control based genetic algorithms for wastewater treatment plants | Genetic algorithm (GA) | Do et al. (2021) | Secondary treatment |
| 6. | Control and soft sensing strategies for a wastewater treatment plant using a neuro-genetic approach | Neural-network-based soft sensor | De Canete et al. (2021) | Secondary treatment |
| 7. | Integrated plant-wide modeling for evaluation of the energy balance and greenhouse gas footprint in large wastewater treatment plants | Integrated plant-wide model | Zaborowska et al. (2021) | Secondary treatment |
| 8. | Quality and cost analysis of a wastewater treatment plant using GPS-X and CapdetWorks simulation programs | GPS-X and Capdet works simulation programs | Abbasi et al. (2021) | Secondary treatment |
| 9. | Modeling and pH control in raceway and thin-layer Photobioreactors for wastewater treatment | Classical on/off control algorithms | Rodríguez-Torres et al. (2021) | In any unit |

(continued)

**Table 5.1** (continued)

| S. No | Title | Method | Author | Treatment unit in which the tool is applied |
|---|---|---|---|---|
| 10. | Model-based strategy for nitrogen removal enhancement in full-scale wastewater treatment plants by GPS-X integrated with response surface methodology | GPS-X integrated with response surface methodology | Cao et al. (2021) | Secondary treatment |
| 11. | Mechanistic modeling of wastewater disinfection by the photo-Fenton process at circumneutral pH | Photo-Fenton, reversible serial *n*-event kinetic model, multiple target—Multiple hit model | Casado et al. (2021) | Tertiary treatment |
| 12. | Modeling of a pulp mill wastewater treatment plant for improving its performance on phosphorus removal | Software BioWin | Bentancur et al. (2021) | Full process |
| 13. | Modeling the dynamic long-term performance of a full-scale digester treating sludge from an urban WRRF using an extended version of ADM1 | Anaerobic digestion model no 1 (ADM1) | Baquerizo et al. (2021) | Secondary treatment |

can cause damage to pumps. The screens are of many types depending upon the opening in them. Some of them are Trash racks which have an opening of more than 36 mm, coarse screens have opening ranging between 6 and 36 mm, fine screens with opening 0.5–6 mm, and micro-strainers (also known as micro screens) with openings ranging from 10 μm to 0.5 mm. Particle size and floc strength are the main parameters that are required for the design of screens (Ljunggren 2006).

At the upstream of the influent flow, a bar screen with a gap of 6–25 mm is used to remove debris that could damage the other process units (Metcalf and Eddy 2003). To avoid the extra expense and need of a communicator, a coarse screen is used for the treatment process. Irrecoverable blockage of the filter media is an issue that has been mentioned in practically every publication. The issue can usually be handled with the cautious operation, monitoring, and correct cleaning solution, yet blockage is by far the most significant disadvantage of micro screening. The usage of screens is obsolete nowadays; instead, scrappers are being used these days. Combining scrapping and dewatered screenings and then pressing is the most efficient method. Furthermore, stainless steel is used for the construction of screens.

#### 5.3.1.2 Grit Chamber

Grit removal systems are used to get rid of grit, i.e., sand, dirt, or other hard solid materials with specific gravities. Because the grit is non-putrescible (microorganisms are not able to decompose it quickly), no additional treatment is necessary before disposal at the final location. Grit is accumulated in vessels or simply in pickup trucks, then transported away at regular intervals. These are usually installed at the headworks of a treatment facility to safeguard the process and the equipment. Though they have an important contribution in the treatment process, there is very less study regarding the modeling and characterization of these units as these are considered to have least impact on the secondary treatment. Moreover, a very less percentage of grit is present in the wastewater, nearly 5–10% (w/w), making them difficult to measure. Grit chambers are typically designed in such a way to eliminate most particulates with a diameter of 0.20 mm or bigger (particles that are retained on a 65-mesh screen) and have a specific gravity of 2.65. At 10 °C, the settling velocity of such particulate is nearly 0.02 m/s, the 0.15 mm sand particles (retained on a 100-mesh screen) are eliminated with a settling velocity of 0.015 cm/s Installing a bar screen on the supernatant discharge from the cyclonic separators helped in increasing the grit removal efficiency (Finger and Parrick 1980). The presence of fats oils and grease (FOG) hinders the grit removal efficiency as they produce a composite particle with the grit, which has different settling velocities (Judd et al. 2017). Particle size and settling velocities are the main characteristics that should be focused on while designing the grit chamber (Plana et al. 2020). The chamber needs to be constructed to scour the lighter particles while allowing the bigger grit particles to settle at the bottom. Rectangular grit chambers with a grit washing system, constant velocity horizontal flow channels, and aerated grit chambers are all examples of technologies that can accomplish this.

#### 5.3.1.3 Equalization Tank

The amount of wastewater entering the wastewater treatment facility plays an important role in the design of the treatment plant. The plant operation gets affected by a varied flow of wastewater. The flow variance has a negative impact on several advanced wastewater treatment technologies. The solids-contact technique, for instance, is vulnerable to a varying flow when it comes to phosphorus removal and chemical precipitation of particles. Precipitation and agglomeration operations would be more efficient if chemicals were fed continuously. If the hydraulic loadings are much more consistent, carbon adsorption is much more efficient. Design, operation, and maintenance grow more expensive when daily flow varies, and several modern treatment strategies become infeasible. An equalization tank helps in getting consistent flow and concentration which increases the suspended solid efficiency (LaGrega and Keenan, 1974). The equalized wastewater has constant velocity, contaminate concentration, and temperature. A fuzzy-based module can regulate the wastewater discharge from the equalization tank (Alferes and Irizar 2010).

### *5.3.2 Primary Treatment*

This is a physical process consists of a circular tank that keeps the wastewater for a significant time for sludge to settle and scum to float in the tank. The concept of primary sedimentation is built on gravity-induced sedimentation. Sedimentation is the process of gravitationally settling the stranded solid particles from the wastewater flow. The process is categorized into two sections: thickening, which involves raising the feed stream's concentration, and clarifying, which involves removing particulates from a comparatively dilute flow. A thickener operates on the gravity settling principle. A vast majority of waste materials remains stranded in sewage. To that goal, halting the discharge of sewage would allow the waste materials to settle. Particle sedimentation is influenced by particle shape, size, and specific gravity, and sewage velocity. The performance of this unit may be affected by the change in hydraulic retention time and the temperature of the influent wastewater (Metcalf and Eddy 2003). During primary treatment, some of the organic and inorganic contaminants are removed from the wastewater, mostly by the sedimentation method. More than 50% of BOD, COD, and TSS get removed in this unit. MLP-ANN (multi-layered perceptron, feedforward backpropagation artificial neural networks) is a modeling tool that could be used for predicting BOD levels of effluent (Rustum and Adeloye 2012). The COD, BOD, and TSS removal efficiency are higher when the surface overflows are higher and, increasing the sludge blanket height increase the $NH_4$ and COD removal efficiency (Borzooei et al. 2017). Primary filtration (PF) can be used as an alternative for primary sedimentation. It uses a pile cloth depth filter (PCDF) and is effective in removing the particulates and organic matter before secondary clarifier (Mansell et al. 2018). A soft sensor could be used for the estimation of TSS in wastewater (Patel et al. 2019). The influent generator model and multivariate statistical analyses can be successfully used in predicting the emission of metals like Cu, Zn, Ni, Cd, Pb, Na, Mg, etc. (Table 5.1). It explains the pattern, source, and effect of human activities on the released elements into the wastewater treatment.

### *5.3.3 Secondary Clarifier*

The effluent from the primary clarifier is further filtered through the removal of residue employing biological treatment methods. In general, contaminant biodegradation is allowed to persist in a region where the microbes have access to an adequate amount of oxygen. This encourages the creation of oxidized products, which are less toxic. Engineers aim to build treatment units with the capability to eliminate sufficient contaminants to avoid substantial oxygen requirements in the receiving stream after release More than 80% of the BOD, COD, and TSS get removed with a significant change in the color of the wastewater. Genetic algorithm (GA), neural-network-based soft sensor integrated plant-wide model, GPS-X and Capdet Works simulation programs, GPS-X integrated with response surface methodology, Anaerobic Digestion Model No 1 (ADM1) are some of the modeling tools that could be used in secondary unit treatment (Table 5.1). GA works on the principle of biological mimicry. It selects the set of parameters that tends to evolve with time. It may help in predicting the fate of certain parameters in a secondary unit of wastewater treatment. GPS-X is a software tool for simulation. It can be used to design the wastewater treatment plant or for upgrading the existing wastewater plant. Anaerobic Digestion Model No 1 is a simulation tool for various anaerobic wastewater treatment processes.

#### 5.3.3.1 Activated Sludge (AS) Method

Activated sludge is described as a suspended mixture of dead and alive microbes in wastewater. An inflow of air "activates" the microbes. Aeration and settling are two different activities that are normally operated in two different basins. Now a days the settling basin has been phased out in favor of membrane separation or some other novel techniques that provide cleared wastewater without the need for a final clarifier. An aeration unit followed by a settling tank (also called clarifier), makes up this sort of system. The aeration unit comprises "sludge," which is a "mixed culture of microorganisms" including mainly bacteria, algae, and other microorganisms. The sludge is continuously stirred and aerated either through compressed air bubblers or mechanical aerators. To supply energy for microbial growth, a few of the substrate will be totally oxidized to non-toxic compounds like $H_2O$, $CO_2$, and other inorganic compounds. The supply of oxygen is the process's most energy-intensive operation. In terms of energy balance, the energy required for pumping the return sludge to the aeration basin, from the clarifier, as well as the functioning of the clarifier are significantly low. When subjected to increased organic and hydraulic loads, this approach may have a few disadvantages. The wastewater enters the unit and combines thoroughly with the microbial culture, which utilizes the organic matter for both growth (creating new microbes) and respiration (primarily yielding water and carbon dioxide). Submerged diffusers continuously provide oxygen for the microorganisms and at the same time mix, the content of wastewater. These tanks generally have a Hydraulic Retention Time (HRT) of about 8 h. These microorganisms break down the organic matter present in the wastewater thus significantly reducing the corresponding BOD and COD. If the wastewater contains pharmaceuticals, it may affect the biological treatment efficiency (Kumar et al. 2019a, b). The study of Kumar et al. (2019a, b) was conducted on pharmaceuticals and personal care products (PPCPs), which is one of the classes of emerging organic contaminants with uncertainty in the effectiveness of MBR, compared to conventional activated sludge, for the removal of PPCPs. To avoid this, Extended Aeration Activated Sludge Process (EASP) could be an effective alternative (Maaroof and Uysal 2017) or using UV/$H_2O_2$ treatment after a biological treatment (Mir-Tutusaus et al. 2021). There are many Antibiotic-Resistant Genes (ARGs), and pathogens present in waste activated sludge that can cause risk to public health. Advanced oxidation processes were reviewed by Miklos et al. (2018). The Electro-Fenton method is efficient in the removal of these pathogens (Wang et al. 2021a, b). In recent years, fluidized bed Fenton (FBR-Fenton) process has gained more attention in treating recalcitrant industrial wastewater. FBR-Fenton combines the effectiveness of homogeneous Fenton and sludge reduction of heterogeneous Fenton (Cai et al. 2021). Increasing the food to microorganism (F/M) ratio and decreasing Solid Retention Time (SRT) and HRT leads to the production of biogas, thus making it a more energy neutral process (Koumaki et al. 2021). Cation-exchange resigns assisted with anaerobic fermentation is very effective in enhancing volatile fatty acids production from waste activated sludge (WAS) (Pang et al. 2021). Sludge blackening is one of the main issues with AS method. The bacteria responsible for this were *Pseudomonas fluorescen*ce, *Hydrogenophaga intermedia*, *Janthinobacterium lividum*, and *Mycolicibacterium pulveris* but surprisingly they have the potential to reduce sulfates to sulfides (Huang et al. 2021). Recently, the use of membrane separation technology alongside bioreactors have opened a new gateway in treating refractory wastewater such as landfill leachate. Anaerobic membrane bioreactor (AnMBR) is a promising technique for leachate treatment due its substantial benefits over other conventional anaerobic and aerobic technologies (Abuabdou et al. 2020).

#### 5.3.3.2 Extended Aeration (EA)

It is a type of activated sludge method but without the application primary sedimentation process but has a high HRT of about 24 h. Aeration, either mechanical or diffused, supplies oxygen for aerobic biological activities and blending to maintain microbes in contact with organic matters. The tank has a prolonged detention time of about 24 h (or even more), enabling the organic particles to settle. This eliminates the requirement for a primary clarification tank, making the procedure cost-effective for small to mid-sized populations with daily flow rates ranging from 500 kl/day to 10 ml/day. Endogenous sludge degradation occurs when the SRT is high. Sludge is allowed to agglomerate in the unit until a point where sludge blanket in the clarification tank reaches a stage where the clarified effluent begins to wash out excessive solids. It could be 6 months or longer between sludge removals. The degradable matter gets removed at a high rate due the long aeration time, moreover, a high SRT encourages the generation of discrete floc, that does not settle, and also, zoogleal floc, that are produced does not settle at lesser SRTs. As a result of the existence of unsettled fine particles, the effluent quality degrades slightly. Diffusers are present for providing the required oxygen to the microorganisms. Aerobic granular sludge (AGS) is a promising alternative since this technology has shown potential for simultaneous organic matter and nutrient removal using smaller bioreactors and consuming less energy (Sepúlveda-Mardones et al. 2019). AGS is a promising technology for mainstream sewage treatment since it has shown stability at organic loading rates (OLRs) tenfold higher than those applied in conventional AS systems (Moy et al. 2002; Show et al. 2012). The total coliform and fecal coliform removal in an intermittent cycle extended aeration-sequential batch reactor (ICEAS-SBR) can be predicted by using the Artificial Neural Network (ANN) (Khatri et al. 2020). Intermittent cycle extended aeration (ICEA) works optimally at a Sludge Retention Time of 10 days, however, removing the SRT further will harm Total Nitrogen and ammonia removal (Latif et al. 2020). Phenol removal efficiency is better in EA than that in AS method and this could be further improved by using activated carbon (Mareai et al. 2020). TOXCHEM model can be used to predict the fate and emission of $H_2S$ in an EA method (Zwain et al. 2020). ICEA sludge produces maximum biodiesel, 18.5% w/w, in comparison to the sludge produced by other biological treatment methods (Hatami et al. 2021). There are a lot of greenhouse gases produced in an EA process. These could be reduced by necessary modifications in the treatment operational parameters, Hydraulic Retention Time (HRT), and Solid Retention Time (SRT) (Yapıcıoğlu 2021).

#### 5.3.3.3 Trickling Filter (TF)

These are bacterial beds where wastewater is trickled from the filters, having attached microorganisms, on the media. In these, extremely high SRTs and microbe concentrations can be obtained. Wastewater is evenly distributed throughout the media and drips below. The substrate is moved to the biological layer connected to the media by mass transport mechanisms. A trickling filter has diverse microflora, yet bacteria have always been the most common microbes accountable for substrate reduction. The microbial film on the media grows until there is inadequate substrate availability and/or the weight of the microbial film cannot sustain the liquid’s shear force that flows over it. The microbial film then suddenly fades away. Due to the sheer clumpy character of faded biofilm, settling issues are uncommon in these. However, in comparison to activated sludge operations, cleared effluent may contain more floating particles, thus lowering the effluent quality. Apart from the complicated attached microbial growth and hydrodynamics, the main benefit of a trickling filtration system is its energy efficiency when compared to traditional activated sludge systems. When appropriately built with a secondary clarification unit and at low organic loads (0.3 kg/day) and high circulation patterns (>150%), trickling filters may even reduce BOD and suspended solids levels with a yield of about 90% or more. Natural convectional currents, generated by temperature variations between the sewage and air, or induced ventilation provide air (oxygen). The media conventionally used are stone media, plastic media, or silica gravel. The filter keeps on rotating for an even spread of effluent on the media. The contaminant removal efficiency was more than 90% in counter-current type TF in comparison to cross-current type which had a contaminant removal efficiency of less than 90% (Yang et al. 2017). A combination of bamboo and biochar could serve as the media for TF (Forbis-Stokes et al. 2018). Other filter media that could be used are granular activated carbon (GAC), Pall rings, zeolite (Forbis-Stokes et al. 2018), and maize cobs, woodchips, and sugarcane bagasse (Ng’erechi et al. 2020). A combination of TF and constructed wetlands could be an effective biological treatment method (Stefanakis et al. 2019). The maximum efficiency of TF is achieved at a substrate column height of 22 cm and 60 HRT (Ng'erechi et al. 2020). During high loads, a bioelectrochemical system (BES) based trickling filter (in which *Geobacter* grows within the layers to generate current) can be used for cost-effective Total Nitrogen (TN) and COD removal without removing the excess sludge (Liang et al. 2020). Trickling filter has an advantage of high efficiency along with high retention time. Odors and vectors are the major drawback of trickling filter.

#### 5.3.3.4 Moving Bed Biofilm Reactor (MBBR)

In this method, the microorganisms grow on the plastic media that remains suspended in the wastewater. It has the same working mechanism as that of AS method. To serve the surfaces on which microbes develop in an MBBR system, polypropylene, polyethylene, or other such material carriers (media) with a specific gravity around that of water (0.94–1.02) are introduced. Aerated mixing keeps the carrier media suspended, while screens restrict them from escaping the reactor. Anaerobic, aerobic, or anoxic treatment can all be done with MBBRs. The specific surface area of the carrier media for microbial growth is determined solely by its internal surface area; the development of microbes on the outside surfaces is limited. An MBBR method requires preliminary screening and grit reduction, but primary sedimentation is not essentially required. The carrier media are typically mounted at a fill fraction range of around 20–67% of the total reactor volume, however, fill fraction range greater than this have also been used. Carrier media will be unable to move freely if their fill volumes exceed 65%. The amount of space taken up by media is a small percentage of the total volume of the tank. For pre-denitrification and post-denitrification processes, MBBRs can be used. One of the major drawbacks of this wastewater treatment method (in comparison to the conventionally used Activated Sludge method) is the energetic cost because of the aeration required for the continuous movement of carrier media Despite its benefits, MBBR efficiency is hampered by scaling of chemical substances, scaling biofilm burden, mineral deposition, and a reduction in surface area. MBBRs have no bulking issues, allowing them to run with more units in series, greater F/M ratios, and a more carefully chosen biomass for each stages of treatment. These have high efficiency when the conditions are saline. MBBR when combined with Microbial Fuel Cells produces bioelectricity which is useful for sustainable energy use (Chen et al. 2020). A study on microbial fuel cell for wastewater treatment and energy recovery is reported by Verma et al. (2021). MBBR system should have high SRT, low dissolved concentration (DO), high COD: N ratio and the carrier media should have high surface area for the effective removal of BOD, TN, and COD (Phanwilai et al. 2020). Model-based soft sensors have been successfully employed in the online monitoring of the wastewater in the MBBR system (Nair et al. 2020). For optimal working of MBBR, the HRT should be about 8 h with a media filling of about 50–60% (Mohammadi et al. 2020). The removal efficiency depends on certain parameters like pH, HRT, Temperature. The MBBR system can be used without a primary clarifier by combining it with disc filtration and coagulation-flocculation (Kängsepp et al. 2020). The MBBR method is effective in TN removal. The average TN removal in MBBR is 63.63% and is due to the presence of bacteria like *Flavobacterium* and *Ottowia* (Yuan et al. 2021). Natural coagulants are recently being researched upon for environment friendly option (Karnena and Saritha 2021; Ang and Mohammad 2020).

### *5.3.4 Tertiary Treatment*

Secondary effluent filtration is called tertiary treatment, and it provides for good water quality. The effluent from the secondary treatment may be subjected to tertiary treatment for further removal of organic matter, disinfection, or color removal to make it look more esthetic. The BOD levels of the effluent from secondary wastewater treatment unit are usually 20 mg/l, with a COD concentration ranging from 60 to 100 mg/l. Household supply of water and emissions into clean water mixing areas require good quality wastewater for reutilization in industrial activities. Oxidation ponds, disinfection units, phytoremediation, constructed wetlands, etc. might be a part of tertiary treatment. BOD, COD, and TSS removal of as high as 95% could be attained after this, but it may make the treatment unit uneconomical. Phytoremediation is a biological process that uses plants to remove contaminants from wastewater. As a consequence, aquatic plants like submerged, floating, and emergent plants are often used in wastewater phytoremediation. Impact 2002+ is used for the Life Cycle Assessment (LCA) of the tertiary treatment unit and the impact of this unit on the environment could be predicted. The other alternate for tertiary treatment units is constructed wetlands (Schierano et al. 2020), the Photo-Fenton method for treating wastewater containing amoxicillin (Díaz-Angulo et al. 2021), Fluidized bed Fenton process (Sun et al. 2021). The Magnox/Ultraviolet light (UVC) process can be used for efficient removal of pollutants under natural condition without the addition of $H_2O_2$ or acid and can be reused (Sciscenko et al. 2021). Ultraviolet radiation has lately proven to be a cost-efficient and non-harmful substitute to the chlorination/de-chlorination method. In comparison to the conventional chlorination/de-chlorination technique, UV light radiation is 12% less expensive to build and operate. This has the extra benefit of avoiding the handling of large quantities of harmful compounds such as sulfur dioxide and chlorine, which decreases the public health risk. The bio-Electro-Fenton system greatly reduced the expenses on wastewater treatment in terms of electric energy consumption and operation costs. The bio-electro-Fenton system is becoming a versatile platform technology and offers a new solution for emerging environmental issues related to wastewater treatment (Li et al. 2018). Much advances in constructed wetland-microbial fuel cells for simultaneous bioelectricity production and wastewater treatment have been reported (Guadarrama-Pérez et al. 2019). A zooplankton-based reactor could be employed as an eco-sustainable tertiary treatment in rural areas for water reuse (Pous et al. 2021). The efficiency of biological tertiary plants such as phytoremediation, constructed wetlands, etc., increases with the increase in the number of macrophytes (Mustafa and Hayder 2021). "$R_{OHO3}$ and $UVA_{254}$ measurements," "photo-Fenton," "Reversible serial *n*-event-kinetic model," "Multiple targets—multiple hit model" are some of the tools used for the tertiary wastewater treatment (Table 5.1). Several modeling tools are suggested in the treatment process. Table 5.1 contains information regarding the use of these modeling tools.

## 5.4 Conclusions

Traditionally the esthetic and oxygen-depleting characteristics of an effluent have been the major focus and hence the measurement techniques in the conventional areas are well known and standardized. Recent development in human activities resulting in enormous quantitative and qualitative change in the wastewater has compelled to search for innovative and economic techniques for eco-friendly disposal of the effluent. The toxic effluent in the wastewater has also affected the behavior of conventional techniques in time and space. Therefore, the research areas have been broadened. Advancement in computerized appliances and modeling ability to analyze the process is huge in the recent past. The focus is also on value-added products along with wastewater treatment processes. Recent work in the last decade has been covered to define the state of the art in the area.

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# Chapter 6
# Nutrient Removal Efficiency of Aquatic Macrophytes in Wastewater

**Sangeeta Sunar, Syed Yakub Ali, Sarmistha Saha, Priti Saha, Pallavi Mukherjee, and Suvanka Dutta**

**Abstract** Eutrophication is an excessive plant-growth process that is one of the serious water pollution problems caused by accelerated nutrient enrichment through runoffs carrying fertilizers, human wastes, etc., which leads to loss of dissolved oxygen and significant deterioration of the water quality and ultimately affecting the aquatic life. Various conventional mechanisms had been introduced to treat nutrient enrichment in water, however, these methods involve high capital for advanced treatments along with the adverse effect of treated chemicals on the aquatic ecosystem. Hence, phytoremediation has emerged as an alternative, eco-friendly, cost-effective technology for treating wastewater compared to conventional technologies. Plants-based in situ solar dependent remediation methods and microbiological techniques are applied in phytoremediation process to reduce the pollutants in natural conditions. The capacity of various aquatic macrophytes for removing nutrients (total Nitrogen and total Phosphorus) from wastewater has been highlighted in the present review paper. Aquatic macrophytic species such as *Eichhornia, Pistia,* and *Typha* have been reported as phytoremediators which are highly efficient in nutrient removal (>90%) from the contaminated water bodies. Therefore, the primary focus of this review article is to assess the current state of phytoremediation as an alternative and advanced technology for the remediation and management of nutrient contaminated water and to highlight the nutrient removal capacity of the aquatic plants.

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**Keywords** Phytoremediation · Eutrophication · Total nitrogen · Total phosphorus · Nutrients · Wastewater

## 6.1 Introduction

Eutrophication has become a serious threat to the aquatic ecosystem in many countries. It leads to a decline in biodiversity, endangering aquatic organisms, nutrient cycle imbalance causing algal bloom, which in turn results in a negative effect on the ecosystem (Elliott and De Jonge 2002). In the aquatic system, greater concentrations of Nitrogen (N) and Phosphorus (P) are found due to the anthropogenic activities like elevated and nonstop release of metropolitan, agrarian and manufacturing wastes into the system (Badr El-din and Abdel-aziz 2018). N and P are the major sources of eutrophication in the water bodies (Frumin and Gildeeva 2014;Smith et al. 1999).A huge amount of nutrients such as N and P is accumulated in the soil due to the usage of the chemical fertilizers (Smith et al. 2007). These nutrients are imperiled to loss by leaching and surface runoff when the soils are saturated. Various ionic forms of N and P result in eutrophication of fresh and marine aquatic ecosystems (Khan and Ansari 2005), which induce the growth and decay of excessive plants algae and death of aquatic fauna, in turn causing degradation of the water quality (Watson et al. 2016). Even rapid urbanization and industrialization have increased the discharge of nutrients to the water bodies from several diffuse and point sources of pollution (Ding et al. 2011). The N levels in the water exceeding 0.3 mg/L and P level above 0.01 mg/L is said to lead to algal bloom in the water bodies (Metcalf and Eddy 1995). Augmentation in eutrophication results in impaired quality and reduction in the availability of potable water (Carpenter et al. 1998). Higher levels of pollutants (such as organic compounds or nutrients and lethal metals) accumulate in the system above permissible limits which make it unfit for intake (Badr El-din and Abdel-aziz 2018). Eutrophication fuels oxygen deficiency in the aquatic system, which creates nasty and harmful fumes, affecting the lives of the fishes, invertebrates (Watson et al. 2015), and the local population, who are directly dependent on the water bodies. Thus, controlling eutrophication using effective remedial technologies for the restoration of the aquatic ecosystem is to be implemented.

## 6.2 Nitrogen Contamination

Nitrogen (N) is present in wastewater in many forms, such as Nitrite ($NO_2$–N), Nitrate ($NO_3$–N), Ammonia ($NH_3$–N), and Ammonium ($NH_4$–N). A high level of nitrogen entering natural waterways can results in toxic condition for wildlife, dissolved oxygen depletion and excessive algal growth. In humans, high nitrate concentrations can cause infant methaemoglobinaemia or blue-baby syndrome (Bashir et al. 2020). Ammonia, the major portion of pollutants in domestic wastewater, is present as ammonia gas and ammonium ions. Ammonium ions is an important element for plant growth but toxic to most lifeforms. Ammonia mostly enters wastewaters mainly from municipal, industrial, agricultural (Constable et al. 2003), and other natural activities such as degradation of organic waste matter, animal waste, atmospheric gaseous exchange, and nitrogen fixation (Alrumman et al. 2016).

In the natural environment, ammonia removal occurs mainly due to nitrification, where ammonia is oxidized to nitrate, volatilization, and uptake by plants and microbes. The plants uptake the nitrate and nitrite, which help in removal of nitrogen or it can be removed through the denitrification process. After denitrification, the dinitrogen gas ($N_2$) or nitrous oxide ($N_2O$) is released in the atmosphere once nitrogen is denitrified. Denitrification is the most important pathway for N removal from the aqueous system in most natural system or wetlands (Wang et al. 2005).

## 6.3 Phosphorus Contamination

In nature, the occurrence of Phosphorus (P) in the surface water is nominal. P is mainly a limiting nutrient ion, i.e., in small quantity (along with N). It is important for the growth of aquatic vegetation and to sustain the aquatic ecosystem. Excess use of chemical fertilizers discharges from industrial and wastewater treatment plants are some of the major sources of P in water bodies. Minute increase in the P entering a water body plays a vital role in the process of eutrophication (Varjo et al. 2003). Lowered light penetration and dissolved oxygen levels, esthetic degradation of water bodies, choking of aquatic lives are some of the major effects of high P concentration in water bodies (Mylavarapu 2009). High nutrient level in water leads to hypoxic conditions which negatively impact the biological activities in the ecosystem.

Several wastewater treatment technologies to remove these pollutants have been developed to address these severe concerns. Available measures help restore and preserve the biological, physical, and chemical characteristics of water bodies. These methodologies are mainly categorized in two primitive groups for purification of wastewater (Nevena and Jovanovic 2005):

1. Conventional methods (biological, physical, and chemical and treatment processes).
2. Alternative methods (self-purification process in natural wetlands).

1. Conventional Treatment Methods

   The conventional methods such as physical treatment like adsorption, biological treatments, chemical, and photochemical treatments like advanced oxidation processes (AOPs) (ultraviolet irradiation, ozonation, UV Fenton’s method, and semiconductor photocatalyst) can considerably eradicate pollutants from the aquatic environment. However, these technologies, specifically the advanced treatment technologies, involve high capital, operational, and maintenance costs (Esmaili et al. 2017; Michael et al. 2013) and further fails to sustain all ecologically conscious societies' demands (Abbasi and Ramasami 1999).For instance, chemical remediation may be advantageous in wastewater treatment due to low energy consumption, cost-effective, and rapid result, although the chemicals used may increase toxicity and result in secondary pollution of the aquatic bodies (Liu et al. 2015). These drawbacks and collateral effects of conventional treatment technologies in aquatic environments paved way for alternative technologies.

2. Alternative Treatment Methods

   In recent years, attention has been budged from just monitoring environmental conditions to the formulations of alternate ways to resolve environmental issues at local and global levels. Phytoremediation, Microbial bioremediation, Constructed Wetlands, root zone treatment are some of the most promising alternative technologies (Lu et al. 2018; Lakshmi et al. 2017; Wang et al. 2010; Vymazal 2011, 2010 and 2007; Stottmeister et al. 2003). These alternative technologies are helpful in the conservation and rejuvenation of the aquatic ecosystems. The alternative treatment technologies such as phytoremediation are highly efficient in terms of nutrient removal (N and P). It is low in maintenance and cost-effective as compared to conventional technologies. Beside this, phytoremediation technologies generate effective byproducts. Adelodun et al. (2020) reported in their study that aquatic macrophytes after phytoremediation showed presence of high value nutritional extract like oleic acid in good amount.

The present review targets on the significance of phytoremediation technologies for nutrient removal from wastewater. In view of the issues related to the increase in nutrients (Total Nitrogen and Total Phosphorus) in the aquatic system, the use and nutrient removal efficiency of aquatic plants in the management of the water quality is discussed in the review.

## 6.4 Phytoremediation

The term phytoremediation ("phyto" means plant in Greek and "remedium" means correct evil in Latin) was coined in the year 1991 (Sachdeva and Sharma 2012). Phytoremediation is the removal and accumulation of contaminants or toxic effects of contaminants from the environment utilizing plants. It includes the mitigation, transfer, stabilization or degradation of pollutants from the environment using plants. These plants have high tolerance in extreme environmental conditions (Adelodun et al. 2020). Phytoremediation has emerged as an eco-friendly cost-effective technology for treating wastewater compared to conventional technologies as plants-based in situ solar dependent remediation methods, and microbiological techniques are applied in the phytoremediation process to reduce the pollutants in a natural condition (Salt et al. 1998; Gupta et al. 2012).

In India, most of the sewage treatment plants are mainly designed for the elimination of Total Suspended Solids (TSS) and Biological Oxygen Demand (BOD) with no adequate treatment facilities for nutrient removal. Phytoremediation seems to be an emerging effective, economically feasible, sustainable, eco-friendly alternate remediation technology that can be used to remove nutrients as a tertiary treatment process in the conventional treatment system. Due to its low cost and minimal negative effects compared to physical and chemical engineering approaches, phytoremediation has proved to be one of the best approaches to clean or remediate contaminated soil and water systems (Mahujchariyawong and Ikeda 2001). Phytoremediation can take place by the following mechanisms:

1. Phytofiltration/ Rhizofiltration

   Phytofiltration or rhizofiltration is a phytoremediation technique which uses hydroponically cultivated plants roots to remediate or remove contaminates from the wastewater through various techniques such as absorption, precipitation and concentration (Arthur et al. 2005). It involves the binding of the pollutants in the root and shoots zones which can be harvested. Both terrestrial and aquatic plants help to precipitate and concentrate the pollutants aqueous sources to low concentration contaminants stored in their roots. Many studies have focused on the removal of N and P from wastewater using this principal phytoremediation technique.
2. Phytoextraction and Hyper-accumulation

   Phytoextraction in wastewater is the availability of aquatic plants to accumulate or remove pollutants from wastewater by concentrating them in the harvestable aboveground biomass (Sachdeva and Sharma 2012). This process requires regular harvesting of the plants in order to lower the concentration of contaminants from the wastewater.
3. Phytostabilization

   This technology uses plants for retention and prevention of further dispersal of contaminants. The contaminants are not removed in this process, however, they are stabilized in the roots or within the rhizospheres of the plants and are then immobilized thereby reducing the innate hazards of the pollutants (Li et al. 2000). The pollutant removal from a particular site is not always feasible; phytostabilization serves as an effective tool in such conditions which results in transformation of the toxic chemicals to an inert condition (Cunningham and Ow 1996).
4. Phytodegradation

   Degradation of the contaminant is one of the significant phases in the course of organic pollutant remediation. The contaminant degradation occurs either through the release of enzymes from the plant roots or through the metabolic activities within the plant tissue (Chigbo and Nnadi 2014). The roots take up the organic contaminants which are then metabolized in the plant tissues and transformed into less toxic substances that can be easily broken down or released in root exudates.

5. Rhizodegradation

   The toxic organic substances are attenuated into less toxic form within the rhizosphere through the biodegradation process of microorganisms which are proficient of releasing enzymes which can carry a biotransformation reaction or other enzymatic transformations (Walton et al. 1994) which is further supported by the plants due to the nutrient potential of plant root exudates. Figure 6.1 shows different phytoremediation mechanisms like Phytofiltration/ rhizofiltration, Phytoextraction and Hyper-accumulation, Phytostabilization, Phytodegradation, and Rhizodegradation.

Recent studies have focused on the use of aquatic macrophytes and rhizomes as potential alternatives for treating and improving the quality of wastewater and agricultural effluents (Saha et al. 2015; Muvea et al. 2019; Mohd Nizam et al. 2020). Removal of N and P from the overlying water is mainly due to the physical and chemical processes associated with the water column and vegetation (Huett et al. 2005). Aquatic macrophytes have the capability to absorb and accumulate the nutrient ions in their tissues (Mahujchariyawong and Ikeda 2001; Su et al. 2019). N and P are directly assimilated in most macrophytes species through their roots, shoots, and leaves (Granéli and Solander 1988). N and P removal using nutrient accumulating aquatic plants has been an alarming topic of research due to their rapid growth, high uptake, and storage capacity (Moore et al. 2016). The mechanism involved in the phytoremediation process for the efficient removal of nutrients from the water body involves (1) selection and application of effective aquatic plant systems, (2) effective nutrient accumulation by the selected plants, (3) harvesting the plant biomasses produced from the

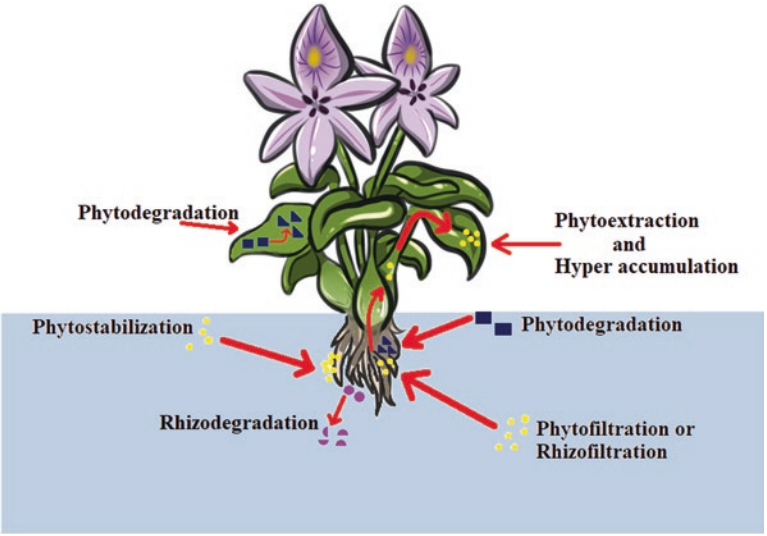


**Fig. 6.1** Phytoremediation mechanisms: phytofiltration/rhizofiltration, phytoextraction, and hyper-accumulation, phytostabilization, phytodegradation, and rhizodegradation

phytoremediation process and their further valuable uses like adsorbent materials, animal feed, biochar, and compost, which might add to clean manufacturing and circular economy efforts (Kurniawan et al. 2021).

## 6.5 Nitrogen and Phosphorus Removal Efficiency of Quintessential Aquatic Macrophytes

Most of the aquatic macrophytes play a substantial role in refining waste water (Xu et al. 2020). High nutrient concentrations are essential for the propagation of aquatic macrophytes, making them the best model to study nutrient profiling of wastewater as they can restore polluted aquatic ecosystems (Martins et al. 2011).Plant species such as water hyacinth (*Eichhornia crassipes*), azolla (*Azolla* sp.), duckweed (*Lemna* sp.), cattail (*Typha* sp.), and water lettuce (*Pistia* sp.) are universally used for wastewater decontamination owing to their high nutrient accumulation capacity from sewage, high tolerance, high biomass production or fast growth and are called phytoremediators.

### *6.5.1 Water Hyacinth*

Water hyacinth (*Eichhornia crassipes*) is a freshwater floating invasive macrophyte with high propagation rate. It doubles in between 5 and 15 days. Figure 6.2 shows general information of Water hyacinth. The nutrient-rich water with 20 mg/L nitrogen (N) and 3 mg/L phosphorus (P) while temperature ranging from 28 to 30 °C with pH value in between 6.5 and 8.5 and salinity <2% (Dersseh et al. 2019) marks the suitable environment for the ideal growth of water hyacinth. This signifies *E. crassipes* as a model nutrient (N and P)-removing plant from wastewater.

Due to inexhaustible growth, *E. crassipes* is the worst intrusive aquatic weed and needs environmental control. Owing to its nutrient absorption efficiency, water hyacinth is used for phytoremediation of sewage as a traditional practice. Harvesting it can serve both purposes-population control and phytoremediation of water bodies receiving huge quantity of nutrients along with sewage treatment (Priya and Selvan 2017) and other industrial uses. The current part comprehends the use of water hyacinth for the removal of nutrients as they act as organic pollutants in wastewater.

Nitrogen-fixing bacteria *Azotobacter chroococcum*, sometimes found to concentrate round the petioles of *E. crassipes* and fix nitrogen if the plant suffers from extreme nitrogen deficiency (Matai and Bagchi 1980). Water hyacinths absorb nitrates from polluted environments. At its maximum growth, one hector of *E. crassipes* could absorb more than 2500 kg-N and 700 kg-P per year (Boyd 1976). The hyacinth gains dry matter till 80 ppm increase in N rate. Removal of total nitrogen (TN) in the range between 60 and 85% from water by *E. crassipes* was

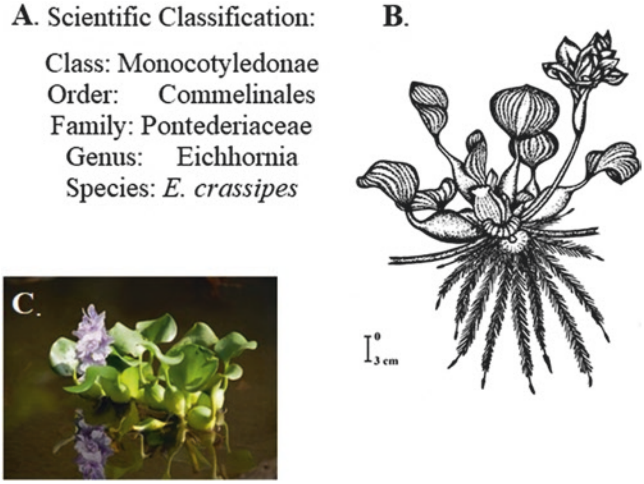


**Fig. 6.2** General information of Water hyacinth: (**a**) Scientific classification; (**b**) illustration showing size in cm (illustration by Dr. Sarmistha Saha); (**c**) Photograph of *Eichhornia* sp.

positively correlated, showing an exponential increase with dry matter gain or increasing canopy cover (Fox et al. 2008).

In case of on-site domestic effluent management, Bio-hedge or engineered attached microbial growth with *Typha* sp. and *Phragmites* sp. have been accounted as more cost-effective phytoremediation technique which lowered Hydraulic Retention Time (HRT) by 33–67% in constructed wetlands and thus improved its performance in eliminating nutrients and organic substance than traditionally using water hyacinth (Valipour et al. 2015). Plants between 6 and 9 weeks growth and 21 days HRT were reported to optimally accumulate TN through assimilation and denitrification process and total phosphorus (TP) by assimilation and sorption mechanisms from wastewaters in the study of Jayaweera and Kasturiarachchi (2004).

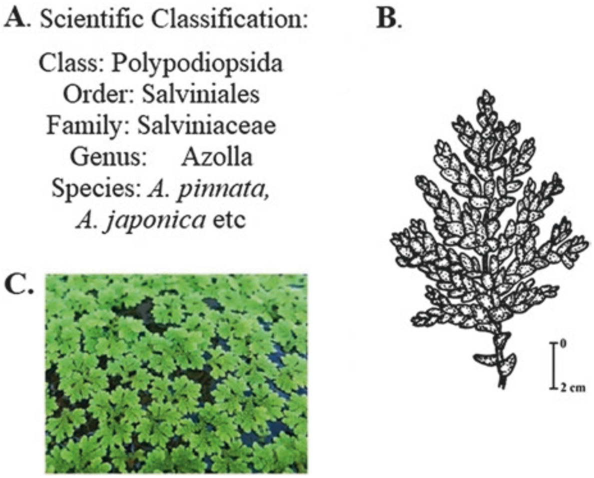
*E. crassipes* showed the highest rate of nutrient removal from the water. Uptake rates of the nutrients (N and P) of the *E. crassipes* is influenced by the concentrations of $NO_3$–N, $NH_4$–N, and $PO_4$–P in the wastewater (Petrucio and Esteves 2000). Water hyacinth was reported to attain the maximum elimination efficiency for TN (89.4%) and $NH_4$–N (99.0%) through a static trial at 28–36 °C water temperature (Xu et al. 2021). The N:P ratio in the aquatic system might influence the absorption capacity of TN and TP. High production rate of *E. crassipes* was recorded at N:P ratio near 3.6 in water (Sato and Kondo 1981). Reddy and Tucker (1983) reported that during the highest biomass production of *E. crassipes*, optimum N and P absorption rates were observed at N:P ratio around 2.3 and 5, respectively. In tropics, *E. crassipe*s was reported to absorb nitrogen and phosphorus more efficiently than *Salvinia auriculata*. Water samples treated with *E. crassipes* showed maximum percent reduction of 85% and 97% for N and P consecutively during higher photoperiod as it showed higher growth in summer (Petrucio and Esteves 2000). In their research article, Martins et al. (2011) reported that accumulated concentration of macronutrients like total nitrogen and phosphorus in leaves of *E. crassipes* is higher while the content of micronutrients was higher in their roots.

Post-phytoremediation, *E. crassipes* can be utilized for various applications. Besides, developing numbers of byproducts like power plant energy (briquette), composting, animal and fish feed, ethanol, biogas, and fiber board making from water hyacinth can partially resolve wastewater treatment issues in industrial or urban areas. Focusing onto the future zero-waste aspects of phytoremediation, the consumption of invasive plants like *E. crassipes* in pollution reduction phytotechnologies can contribute to its sustainable control in parallel with wastewater treatment (Rezania et al. 2015).

### 6.5.2 *Azolla*

One of the major macrophytic species is Azolla, which is used to treat wastewater by using phytoremediation technique. Azolla has a symbiotic association with bacteria residing in leaf cavities, diazotrophic, and nitrogen-fixing cyanobacteria cavities (Forni et al. 2001; Sood et al. 2008; Sood and Ahluwalia 2009). The symbiotic association with the nitrogen fixing cyanobacteria is one of the major advantages for treating wastewater with high level of nitrogen. Therefore, it is one of the most promising macrophyte for treating wastewater through phytoremediation. Figure 6.3 shows general information of *Azolla* sp.

*Azolla pinnata* was recorded to treat the domestic wastewater in the free water surface constructed wetlands. A study was conducted to treat the constructed wetland in Akure, Nigeria. The result of this study indicates that the reduction of TN



Class: Polypodiopsida
Order: Salviniales
Family: Salviniaceae
Genus: Azolla
Species: *A. pinnata*, *A. japonica* etc

**Fig. 6.3** General information of Azolla: (**a**) Scientific classification; (**b**) illustration showing size in cm (illustration by Dr. Sarmistha Saha); (**c**) photograph of *Azolla* sp.

was from 900 ± 20.45 mg/L to 209 ± 15.23 mg/L during dry season and 504.43 ± 10.23 mg/L to 157 ± 12.12 mg/L during wet season. The experiment established that a higher amount of ammonia was removed from the wastewater, which may be due to the plant's uptake of ammonia or nitrate ions. These ions are fixed by the nitrate fixing bacteria, which resides in symbiotic association with this macrophyte. Moreover, the removal for Total phosphate by *A. pinnata* from the municipal wastewater was observed in a range of 12.5 ± 0.67–2.95 ± 0.23 mg/L in the dry season and ranged 7.68 ± 0.67 mg/L–1.76 ± 0.12 mg/L in wet season (Akinbile et al. 2016). Apart from this, *A. pinnata* was recorded to treat dairy, domestic and municipal wastewater by Sreelakshmi & Ashokan (2020). It helps in reduction of N and P from 30 mg-N/L to 7.1 mg-N/L, 3.9 mg-P/L to 0.5 mg-P/L in dairy wastewater, 70 mg-N/L to 14 mg-N/L, 45 mg-P/L to 2 mg-P/L in domestic wastewater, and 12 mg-N/L to 0.9 mg-N/L, 20 mg-P/L to 1 mg-P/L in municipal wastewater. Therefore, this study documented a removal efficiency of 76–93% of N and 87–96% of P by *A. pinnata*. Even, one of the researches also states that the eutrophication of the wastewater can be controlled by using *A. pinnata* in the system. The results confirm that the *A. pinnata* helps in reduction of ammonia and phosphorus from the wastewater in 14 days (Acero 2019).

Apart from the *A. pinnata*, *A. filiculoides* was used to treat the anaerobic digested swine wastewater. It was found that this species has high efficiency to absorb N and P from the wastewater. It showed 100% removal of ammonia and 83% phosphate removal from the wastewater. Similarly, recovery of nitrogen and phosphate was observed while verifying the treatment efficiency of this species in the tropical semiarid regions of Ethiopia. The wastewater from the textile, distillery, and domestic source was mixed in the ratio of 3:1:18 and set for treatment for 28 days in a batch system with *A. filiculoides*. The P and N removal efficiency was observed to be 98% and 93.2%, respectively (Amare et al. 2018). The study carried out by Costa et al. (2009) also revealed that the *A. filiculoides* is a better system to remove phosphate and nitrogen from the urban wastewater in comparison to other small aquatic plants. The results showed that 23.1 mg/m$^2$/day of phosphorous and 194.1 mg/m$^2$/day of nitrogen were up taken by Azolla from the wastewater.

The other Azolla species as Japonica and Caroliniana are also considered as good system to remediate phosphorous and nitrogen. *Azolla caroliniana* fixed 0.99 ± 0.34 kg/ha/day of Nitrogen and 43 ± 15 mg/m$^2$/day of Phosphorous (Reddy and DeBusk 1985). It was also recorded that a considerable amount of the nutrients (>50% of N and P) are removed from swine lagoon sewage as well as fish farm sewage by *Azolla japonica* (Song et al. 2012).

The research revealed that after wastewater treatment, the Azolla biomass becomes rich in nutrients due to uptake of the nutrients from the wastewater. These macrophyte biomass can be effectively used as biofertilizer (to enhance the soil fertility), which can be used as green manure in the agricultural field, feed supplements for aquatic as well as terrestrial animals. Even it can be used for production of biogas, carbon-rich bio-solids, and liquid petrochemicals (Jangwattana and IWAI 2010; Amare et al. 2018; Azab and Soror 2020).

The main advantage of using Azolla in comparison to other macrophytes is that it can treat wastewater where nitrogen becomes a limiting growth factor. This is due to its symbiotic co-existence with nitrogen fixing bacteria cyanobacterium. The cyanobacteria help to fix atmospheric nitrogen, which helps in the growth of the macrophyte (Azab and Soror 2020). Various studies were taken up to estimate its impact on the nitrogen present in wastewater, since the cyanobacterium also fixes nitrogen. However, it was found that up to 34 mg/L of ammonia in wastewater does not inhibit the growth or treatment efficiency (Costa et al. 2009).

### 6.5.3 Duckweed

Duckweed (*Lemna minor*) is a small, free-floating monocotyledons plant having no stem but one to four oval leaves or fronds, each having three veins with little air space and solitary root (Hu et al. 2020). Figure 6.4 shows general information of Duckweeds. It grows in still and almost motionless water in many regions of the world except Arctic and Antarctic regions (Zhao et al. 2014; Muradov et al. 2014). Frick (1985) stated that the fronds of *L. minor* double within 1.4 days. The phytoremediation capacity of duckweed is related to the growth status of the species, the category of pollutants and their concentrations. Duckweed can grow in rich organic matter and nutrient condition. It entails temperature of 6–33 °C, pH of 5–9, and pond depth of 0.5 m (Hasan et al. 2009; Leng et al. 1995). For development, duckweed require 60 mg/L nitrogen and around 1 mg/L (minimum) phosphorous (Ekperusi et al. 2019).

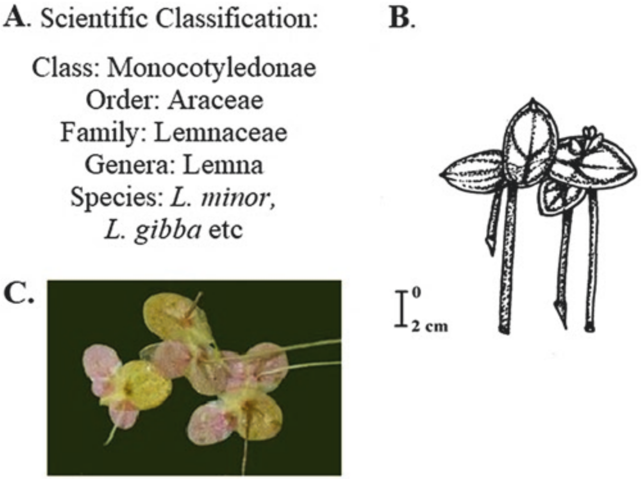


**Fig. 6.4** General information of Duckweeds: (**a**) Scientific classification. (**b**) Illustration showing size in cm (illustration by Dr. Sarmistha Saha); (**c**) Photograph of *Lemna* sp.

Duckweeds can nurture wastewater effectively and transform biodegradable impurities directly into valuable materials, like protein-rich feed (Oron et al. 1985). Various studies shows that duckweeds grow fairly on municipal sewage water (Körner and Vermaat 1998; Ozimek 1983; O'Brien 1981; Culley Jr and Epps 1973), swine wastewater (Hu et al. 2019), diary wastewater, livestock wastes (Myers 1977; Hu et al. 2020), and under laboratory conditions on several pollutants such as $NH_3$–N, detergents, $PO_4^{3-}$ and on anaerobic water (Agami et al. 1976; Wolverton and McDonald 1979).

Primary and secondary treatment only caused the reduction of 50% of nutrients from whereas duckweed resulted in 79.39% depletion of nutrients (Priya et al. 2012). Duckweeds were recorded to eliminate 98% and 98.8% ions of total nitrogen and phosphorous when DO level is amplified (Mohedano et al. 2012). Körner and Vermaat (1998) reported that Duckweed (*Lemna gibba* L.) was accountable for the total N-loss of around 30–47% and 52% of the total P-loss from wastewater in laboratory test. Here the exceptional output data stated by the authors that duckweed was very effective in depletion of organic contaminants in water body, specifically for the management of wastewater discharged from agrarian and industrial manufacturing plants. Duckweed require sample amount of nutrients to nurture its growth and development, which is useful for nitrogen and phosphorus retrieval from *Lemna* sp. It is reported to reduce 36.15% phosphorus from wastewater (Sudiarto et al. 2019; Xu and Shen 2011). Cheng et al. (2002) had reported that *Spirodela punctata* helped in recovering phosphorus and nitrogen from synthetic artificial medium (SAM) which was articulated in a manner to resemble conventional swine lagoon water. It is evident from the result that duckweed growth was well supported by high concentration nitrogen and phosphorus condition($NH_4$–N of 240 mg/L and $PO_4$–P of 31.0 mg/L). The maximum duckweed growth rate attained was reported to be 1.33 g dry biomass/$m^2$–hand maximum nutrient uptake rate were 0.995 mg/L-h for N, 0.129 mg/L-h for P.

All duckweed species are not effective for phytoremediation. Oron et al. (1985) reported that *Wolffia arrhiza* performed poorly and did not grow sufficient plant matter for stocking the wastewater lagoons compared to *Spirodela polyrrhiza* and *Lemna gibba*. Bergmann et al. (2000) compared three geographic isolates of duckweed, *S. punctate, Lemna minor,* and *Lemna gibba,* to treat sewage of swine lagoon and inferred that when grown on 50% swine lagoon wastewater *L. minor* and *L. gibba* showed robust growth with effective nutrient reduction (86.0 mg/L of $NH_4$–N and 25.3 mg/L of $PO_4$–P). Another comparative study conducted by Yilmaz and Akbulut (2011) of individual potentials of duckweed species showed *L. minor* to be little more efficient than *L. gibba* in sewage, whereas *L. minor* was quite efficient than *S. polyrhiza* and *L. punctate* in swine wastewater. Even though duckweeds share an outstanding and representative familiarity in the Lemnaceae family, there are several species having diverse capabilities to acclimatize to an array of contaminants or stress in the ecosystem. With better adaptive potential *L. minor* collects and reduce contaminants in the surrounding ecosystem in comparison with the other species of duckweed. The mixture of different duckweed species were highly efficient for the recovery of nutrients from polluted waste (Ekperusi et al. 2019).

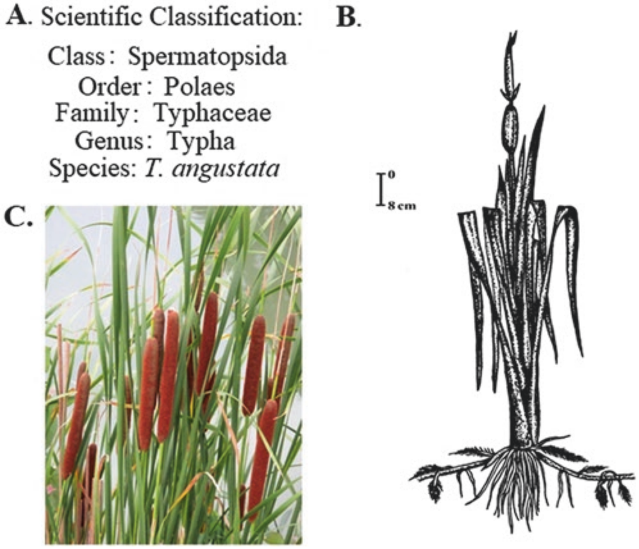
Chen et al. (2018) reported that removal efficiencies of TP (90.8%) and TN (99.1%) from wastewater by combined species of duckweeds as *Spirodela polyrhiza*, *Landoltia punctata,* and *L. minor* were higher and more efficient than application of a single duckweed species.

The removal of nutrients can be evident from the increased growth and protein accumulation (35%) (Ziegler et al. 2015; Mohedano et al. 2012) in duckweed species indicating nutrients uptake by plant from the wastewater for biomass development (30% increased within 21 days) (Saha et al. 2015). Post-harvest duckweed biomass, as a derivative of the swine wastewater pond treatment, might act as protein-rich (ranging from 15 to 45%)supplement for animal fodder (Landolt 1986; Landolt and Kandeler 1987).

Duckweed mat together with the bacteria and algae might boost purification of wastewater by the process of anaerobiosis caused by bacterial decomposition in the water, which is then maintained by the duckweed mat by preventing re-aeration(Oron et al. 1985; Körner and Vermaat 1998).

### 6.5.4 Cattails

Cattails (*Typha* sp.) is an aquatic or semi-aquatic herbaceous flowering plant belonging to Typhaceae family. It is an emergent species growing abundantly in the wetland habitats and in the banks of ponds and lakes. Figure 6.5 shows general information of Cattails. This plant has 12–16 narrow, flat, glabrous leaves that grows



A. Scientific Classification:

Class: Spermatopsida
Order: Polaes
Family: Typhaceae
Genus: Typha
Species: *T. angustata*

**Fig. 6.5** General information of Cattails: (**a**) Scientific classification; (**b**) illustration showing size in cm (illustration by Dr. Sarmistha Saha); (**c**) photograph of *Typha* sp.

from 1 to 2 m in height when mature, and rhizomatous roots which are long and well-built (Grace and Harrison 1986; Kumar et al. 2013). The flowers are unisexual developing into racemes. On maturation, the heads form fluffy structure and the small seeds attached to the hairs disperse by wind and is transported by animals and humans. Due to its extensive dispersion, *Typha* sp. that originated in Europe is now distributed extensively across the world.

Various studies on phytoextraction of N and P from effluent by *Typha* sp. have been reported. de Queiroz et al. (2020) showed that the reduction of TN and TP by *T. domingensis* and combination of *T. domingensis* and *Eleocharis interstincta* is much more efficient for phytoremediation of dairy industry wastewater in constructed wetland with application of the plant as compared to non-vegetated constructed wetland. The reduction mean exhibited by *Typha* sp., combination of *Typha* and *E. interstincta* and non-vegetated constructed wetland were 47%, 48%, and 15.4%, respectively, for N and 34%, 43%, and 13.8%, respectively, for P.

Gebeyehu et al. (2018) assessed phytoremedial capacity of *Typha latifolia* grown in brewery wastewater using hydroponics technology to remove nutrients. The Typha containing hydroponic treatment units performed well with mean removal rates of 58%, 69%, 51%, and 54% for $PO_4^{3-}$TKN, $NO_3^-$N, and $NH_4$–N consecutively as compared to the control unit without *Typha* with corresponding removal rates of 41%, 25%, 26%, and 34% under 5 days hydraulic retention time. Another study conducted by Di Luca et al. (2015) in 10 L reactors with 4 kg of sediment spiked with 100 mg P-$PO_4^{3-}$/L (P100) and 500 mg P-$PO_4^{3-}$/L (P500) found that $PO_4^{3-}$-P removal was much higher in vegetated (with *Typha domingensis*) (68.1% for P100 and 61.0% for P500) than in reactors without Typha for both P treatments (51.8% for P100 and 34.1% for P500). Akratos and Tsihrintzis (2007) used medium gravel as base material in constructed wetlands for cultivation of *Typha latifolia*. In their experiment it was revealed that *Typha* can removal 66.8% and 66.9% of TKN and $PO_4^{3-}$, respectively, from Synthetic wastewater. However, some researcher observed a small increase in the $NO_3^-$ concentration in the wetlands planted with cattails (Huang et al. 2000; Akratos and Tsihrintzis 2007) which may be due to the vigorous nature of the plant and availability of sizeable zone for nitrification.

Accumulation and storage of high amount of N and P mainly in the aboveground parts of *Typha* sp. (weight ranging from 0.21 to 1.8 kg dry weight/m$^2$ (DW/m$^2$) has been evaluated in multiple studies (Jeke 2018; Gebeyehu et al. 2018; Salem et al. 2017; Maddison et al. 2009). Gebeyehu et al. (2018) in their study comprising of triplicate hydroponic bioreactor treatment units showed that the dry weight of biomass in these units was 0.61–0.78 kg DW/m$^2$. The nutrient accumulation in the harvested biomass was found to be 2.43–2.87 g P/kg DW and 16.47–21.17 g N/kgDW, whereas 10.06–18.21 g N/m$^2$ and 1.48–2.47 gP/m$^2$ are the estimated nutrient enrichment in the aboveground dry biomass of *Typha* sp. harvested per unit area. Tanner (1996) also reported similar results with aboveground nutrient concentrations in the harvested plant biomass extending from 1.3 to 3.4 g P/kgDW and 15 to 32 g N/kgDW. Harvesting season and harvest frequency has proved to exert effect on N and P removal by *Typha* sp.as evaluated by Jeke (2018) in their study. The study showed that a single harvest per season resulted in biomass yields of

0.58–0.6 kg/m$^2$ per year and nutrient accumulation of 36.7 g/m$^2$of N and 5.6 g/m$^2$of P over 4 year study period. As compared to this, there was 50–60% decrease in phytoextraction of N and P when harvested twice per season.

As the studies suggested, nutrient accumulation is proportional to the pollutant removal from the wastewater together with increased dry weight yield in plants. Therefore, the ability of the plant to nutrient reduction in sewage is a function of biomass production and nutrient uptake which can then be used for various value additions as per its characteristics. Solano et al. (2004) has reported that biomass of *T. latifolia* might be used to generate energy. When utilized properly, the nutrient content of wastewater can serve to be a valuable resource whereas untreated wastewater discharged directly to receiving water bodies can cause eutrophication and ecological damage (Gebeyehu et al. 2018).

Various factors play a significant role for phytoremediation of nutrients from wastewater by *Typha* sp. Akratos and Tsihrintzis (2007) observed that temperature, affecting microbial activity and vegetation function, significantly influences the phytoremediation capacity of the plant. In the study, one of the constructed wetlands showed the mean TKN and ammonia removal below 15 °C temperature as 58.5% and 37.9%, respectively, which increased to 73.9% and 69.1%, respectively, above 15 °C temperature. Mean removal of TP and P-$PO_4^{3-}$were 41.8% and 50.7%, sequentially below 15 °C temperature and 79.2% and 70.1%, respectively, above 15 °C which is mainly due to plant decay followed by organic breakdown and thus release of organic phosphorus in the unit, together with the release of phosphorus through precipitation (Kadlec and Knight 1996, Kadlec and Wallace 2008). As per the study conducted by Jeke (2018), phytoextraction of N and P reduced by 63–85% when *Typha* is harvested in November or April as compared to August.

Nutrient removal efficiency of *Typha* sp. is significantly affected by Hydraulic Retention Time (HRT). Akratos and Tsihrintzis (2007) in their study reported that, all the constructed wetland units showed considerably different removal efficiencies with 6-days HRT and 8-days HRT when temperature was above 15 °C (TKN removal for HRT of 6-day was 44.8% and for HRT of 8-day was 80.2%). No such difference occurred considering HRT of 8-day and HRT of 14-day (TKN reduction of 80.2% and 78.9%) but greater removal efficiencies were detected for HRT of 20-day (85.9%removal of TKN) as compared to HRT 14-day (78.9% removal of TKN). Even in favorable temperatures, HRT of 6-day did not yield appreciable removal, but comparatively high elimination was achieved for HRT of 8-days and above. At below 15 °C temperature, both HRT of 8-day (mean removal of TKN was 50.0%) and HRT of 14-day (mean removal of TKN was 53.5%) did not show good removal but HRT of 20-day resulted in comparatively substantial nutrient removal (83.9% mean removal of TKN and 68.9% mean reduction of ammonia). These results implicate that at high temperature, nitrogen removal efficiency of *Typha* sp. is considerably good at HRT 8-day, but it no longer remains adequate at low temperatures therefore requiring a higher residence time for adequate nutrient removal.

The removal efficiencies for $PO_4^{3-}$-P and TP for HRT of 6, 8, 14, and 20 days depicted a parallel picture as N (mean removal of $PO_4^{3-}$-P at HRT 6-day, HRT 8-day,HRT 14-day and HRT 20-day were 33.6%, 56.3%, 76.5%, and 88.1%, respectively). For, it seemed that only there was low reduction of $PO_4^{3-}$-P and total P ($PO_4^{3-}$-P mean removal was 49.3%) for 6-day HRT when temperature was kept above 15 °C. HRT 8-day and 14-day showed high reduction of $PO_4^{3-}$-P (mean removal of $PO_4^{3-}$P was 81.1% at 8-day together with 90.3% at 14-day) under similar temperature condition. For temperature below 15 °C, it was found that 8-day HRT showed reduced $PO_4^{3-}$-P removal (mean removal of $PO_4^{3-}$-P was 31.5%) whereas HRTs at 14-day and 20-day showed higher reduction of $PO_4^{3-}$-P and total P (mean removal of $PO_4^{3-}$-P is 67.7% for HRT14-day and 78.0% for HRT 20-day). From the results it was therefore inferred that above 15 °C temperature, a HRT 8-day is satisfactory, whereas below 15 °C temperature, greater hydraulic retention time like HRT 14-day or HRT 20-day was necessary.

Newman et al. (1996) and Grace (1989) reported that the dominance of *Typha* sp. is supported by shallow water depths (i.e., 0.2–0.3 m) and nutrient enrichment in water bodies. Although *T. domingensis* and *T. latifolia* can rise at water depths ranging between 0 and 115 cm, but increased flowering frequency and shoot density can be exhibited in shallow water depth (Grace 1989). With increasing depth of water, the shoot height of *T. domingensis* increases and it produces longer buta smaller number of ramets along with reduced flowering incidence. Also, depth of water is inversely proportional to the anchorage capacity of plants as it caused decrease in the biomass allocation to roots and rhizomes (Grace 1989).

### *6.5.5 Water Lettuce*

Water Lettuce (*Pistia stratiotes* L.) is a fresh water floating monocotyledonous macrophyte (Walsh and Maestro 2014). *Pistia* sp. is a South American native species which primarily propagated through vegetative growth (Hussner et al. 2014; Hill 2003). Even though being an aggressive invasive species, water lettuce has been extensively used in wastewater phytoremediation in the tropical and subtropical regions (Putra et al. 2015; El-Gendy et al. 2005; Karpiscak et al. 1994) due to its fast growth rate (Reddy and Sutton 1984), higher P and N reduction efficiency (Lu et al. 2010) and high productivity (Chen et al. 2015) as compared to other native species. During peak growing period the water lettuce are known to accumulate large amount of nutrients (Reddy and DeBusk 1985; Porath et al. 1979). Water lettuce is a winter intolerance plant with a minimum growth at 15 °C and highly sensitive to cold temperature which significantly affects their performance due to which they may not be suitable for temperate or frigid areas (Clough et al. 1987). Temperature below 10 °C and lower solar radiation during the rainy seasons limits the growth rate and other microbial activities thereby hindering the phytoremediation efficiency. Figure 6.6 shows general information of Water lettuce.

Water lettuce doubles its mass in just 5 days and has its mass multiplied nine (9) times in less than a month. This evolution indicates that the maximum period to allow this plant in the system is 25 days (Gupta et al. 2012). It is capable of

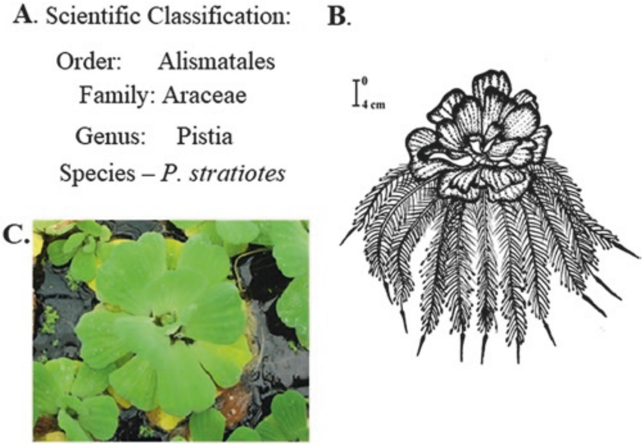


**Fig. 6.6** General information of Water lettuce: (**a**) Scientific classification; (**b**) illustration showing size in cm (illustration by Dr. Sarmistha Saha); (**c**) Photograph of *Pistia* sp.

accumulating huge nutrients content during peak growth (Fonkou et al. 2002). Due to its rapid productivity and high rate of decay, the efficiency is linked to its careful management through periodic harvesting (mostly 25 days). It is recorded to withstand high salinity conditions (Haller et al. 1974) but growth is limited at high COD levels Sooknah and Wilkie 2004.

Kumar and Deswal (2020) in their study compared the phosphorus reduction efficiency of water hyacinth, duckweed, water lettuce and watermoss (*Salvinia* sp.). In their study it is recorded that, the P removal efficiency of water lettuce is maximum (80.04% on Day 15) as compared to others. However, after Day 15 an increase in the P concentration was observed which might be due to the decay of plant roots and leaves. Treatment of wastewater from parboiled rice mill using water lettuce in a lab-based batch study having high chemical oxygen demand (COD), P, N and low pH was conducted by Mukherjee et al. (2015). The results showed a high efficiency in removal of $NH_4$–N (97%). Sooknah and Wilkie (2004) reported varying reduction efficiency of $NH_4$–N, TKN and TP as 99.2%, 87.6%, and 64.2%, respectively, during treatment of wastewater from flushed dairy manure that are anaerobically digested. Schwantes et al. (2019) evaluated the potential of water lettuce for post-treatment of domestic wastewater in their 42 days experiment. The results demonstrated efficiency removal of total N and total P by 100%. Awuah et al. (2004) observed a total removal of Nitrate ($NO_3$–N), Total phosphorus (TP), and $NH_4$–N by 70%, 33%, and 95%, respectively, in their study of bench-scale wastewater treatment system. Aoi and Hayashi (1996) in their study reported the total consumption of ammonium ($NH_4$–N) present in the system before switching to $NO_3$–N as source of nitrogen by water lettuce. Gonzaga Henry-Silva and Monteiro Camargo (2008) observed 69.9% reduction efficiency of water lettuce. Shah et al. (2014) reported an average P removal of 10.69% (Initial P concentration 2.1 mg/L) using water lettuce. Akinbile and Yousoff (2012) reported a maximum reduction of 92.85%, 57.13%, 70.33%, 96.12%, and 72.82% in Total Kjeldhal Nitrogen (TKN), $NO_3$–N, $NO_2$–N, $NH_4$–N, and P, respectively, in aerated and 85.71%, 83.34%, 70.67%, and 69.64%, respectively, in non-aerated container using water lettuce in third week of the treatment during the 30 days experiment. Similarly, Niveth et al. (2016) also reported an average reduction in the phosphorus concentration by 81.3% (Initial P concentration 23.4 mg/L) in domestic wastewater using water lettuce. Similarly, a maximum phosphate and nitrate removal efficiency of water lettuce (81.2% and 83.6%, respectively) in domestic wastewater was recorded by Mustafa and Hayder (2021; 2020). A Nitrate removal efficiency of 31–51% was reported by Ingersoll and Baker (1998). Lu et al. (2010) reported an improvement in the water quality of a pond by phytoremediation treatment using water lettuce. A reduction of 18–58% compared to the control plot was found in ortho P, total dissolved P and total P (Lu et al. 2011). A reduction in the $NH_4$–N, $NO_3$–N, and TKN was also reported.

In the previous decade, macrophytes like water primrose (*Ludwigia adscendens*), water chestnut (*Trapa natans*), Water spinach (*Ipomoea aquatica*), Common rush (*Juncus effuses*), Parrot's feather (*Myriophyllum aquaticum*), coontail (*Ceratophyllum demersum*), giant salvania (*Salvinia molesta*), Powdery alligator-flag (*Thalia dealbata*), Indian shot (*Canna indica*), and Reed (*Phragmites australis*) are also reported to emerge as potent wastewater purifying agent. Table 6.1 represents the details of some studies using these macrophytic species.

## 6.6 Conclusion

In this paper, the potential of various aquatic macrophytic species commonly used for phytoremediation in terms of nutrients removal and purification of eutrophic water has been explored. The review elucidates usefulness of aquatic macrophytes in treating eutrophicated wastewaters. The study indicates that the five aquatic species namely, water hyacinth, water lettuce, azolla, duckweeds, and cattail can be utilized as effective phytoremediators in nutrient enriched wastewater treatment. The phytoremediation technologies prove to be economic, low maintenance sustainable tool for the reduction of N and P from sewage water. For overall efficiency, proper periodic harvesting of dead macrophytes is recommended as decomposition of the dead species contributes to nutrient enrichment in the wastewater. Various by-products from the harvested biomass might act as resource to help in economy generation, while, reducing secondary waste generation. Therefore, further advance research in this field should be employed for wastewater reclamation. Current study will help to prepare efficient model to execute and manage wastewater treatment system using aquatic macrophytes in warmer geographical regions. Overall, the study reveals that this green remediation technology can be a promising ecological approach for nutrient removal from wastewater to assess and control water pollution.

**Table 6.1** Nutrient removal efficiencies (%) of selected macrophytes used in phytoremediation

| Sl. No. | Common name | Scientific name | Lifeforms | Family | Effluent type | Removal efficiency (%) | | References |
|---|---|---|---|---|---|---|---|---|
| | | | | | | TN | TP | |
| 1. | Water primrose | *Ludwigia adscendens* (L.) H. Hara | Rooted floating leaves | Onagraceae | Swine manure wastewater | 79.04 | 95.90 | Xu et al. (2020) |
| 2. | Water chestnut | *Trapa natans* L. | Rooted floating leaves | Trapaceae | | 84.05 | 88.72 | |
| 3. | Water spinach | *Ipomoea aquatica* Forsk. | Rooted floating leaves | Convolvulaceae | Palm oil mill wastewater | 82.7 9 (as $NH_3$–N) | – | Sa’at and Zaman (2017) |
| 4. | Common rush | *Juncus effuses* L. | Emergent | Juncaceae | Nutrient enrichment through agricultural runoff | | 77 | Menon and Holland (2013) |
| 5. | Parrot’s feather | *Myriophyllum aquaticum* (Vell.) Verdc. | Submerged | Haloragaceae | Spiked | 80.2 | 89.7 | Feng et al. (2018) |
| | | | | | Swine wastewater | >30.1 | >39.8 | Cui et al. (2021) |
| 6. | Coontail | *Ceratophyllum demersum* L. | Submerged | Ceratophyllaceae | Nutrient polluted waterbody | 55.7–64.95 (as NH3) | 63.49–73.33 | Dai et al. (2012) |
| 7. | Giant salvania | *Salvinia molesta* D. Mitch. | Free floating | Salviniaceae | Ricemill wastewater | | 61.38 (as P) | Kumar and Deswal (2020) |
| 8. | | | | | Domestic wastewater | 90.47 (as $NH_3$)<br>92.1 (as $NO_3$) | 82.7 | Mustafa and Hayder (2020) |
| 9. | Powdery alligator-flag | *Thalia dealbata* Fraser ex Roscoe | Emergent | Maranceae | Domestic sewage | 18 | 37 | Zeng et al. (2020) |
| 10. | Indian shot | *Canna indica* L. | Emergent | Cannaceae | | 27 | 47 | |
| 11. | Reed | *Phragmites australis* (cav.) Trin. ex Steud. | Emergent | Poaceae | Polluted river | 60.74 | 47.76 | Wu et al. (2011) |

**Declarations**

**Ethics Approval and Consent to Participate**: Not applicable.

**Consent for Publication**: Not applicable.

**Code Availability:** Not applicable.

**Availability of Data and Materials:** Not applicable.

**Competing Interests:** The authors declare that they have no competing interests.

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# Chapter 7
# Microbial Degradation of Wastewater

**Nupur Raghav, Rajesh Nigam, Shivangi Mathur, Deeksha Singh, and Rajiv Ranjan**

**Abstract** Water is essential for varied human activities, its quality and quantity are attracting increasing attention around the world because of tremendous population expansion, rising socio-economic growth trends. Industrial, municipal, domestic, and agricultural wastewater is discharged directly into surface water that has the potential to harm the natural aquatic environment and biotic life, posing serious health risks to humans. Recycling and reusing wastewater are a long-term solution to the rapid increase in water pollution and scarcity. As a result, bioremediation plays a key role in recycling hazardous wastes into a form that other organisms can use. There have been several chemical and physical approaches to wastewater treatment, but biological treatment processes are more effective in reducing the majority of harmful pollutants found in wastewater which is low cost and environmentally friendly of all the physicochemical treatment processes. In this process, native microorganisms such as bacteria, fungus, and algae remove heavy metals, pesticides, suspended solids, dissolved solids, nitrate, phosphate, heavy metals chemical oxygen demand (COD), and biological oxygen demand (BOD) from wastewater. This chapter emphasizes on the relevance of fungi, algae, and bacteria in wastewater pollutants bio-remediation.

**Keywords** Bioremediation · Sustainable · Contaminants · Bacteria · Fungi · Algae

## 7.1 Introduction

Developing countries have witnessed escalated urbanization and industrialization. Substantial amount of wastewater is generated by municipal corporations (MCs), houses, urban local bodies (ULBs), and industry, which is then released into nearby

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water bodies without being properly treated, resulting in water pollution. Wastewaters of different sources discharged directly into rivers have the potential to disturb natural aquatic ecosystems and biota, and pose major health hazards (José et al. 2015). Due to the high value and energy consumption, hazardous by-product manufacture, and sludge generation, all of which cause secondary pollution, researchers are looking for more cost-effective alternative treatment methods.

For biodegradation of the wastewater contaminant, biological treatment is considered as more efficient, economic, and environmentally friendly method of contaminant clean up in contrast with the physiological and chemical analysis (Guimarães et al. 2018). Tertiary filtration and advanced chemical analysis facilities, like activated carbon filtration or chemical precipitation techniques, are typically required to eradicate dispersed microorganisms from effluent before reutilization or discharge into water reservoirs (Abdel-Raouf et al. 2012). Bioremediation could be considered as cost-efficient and eco-friendly way to recover polluted water bodies. In this ground-breaking strategy, microorganisms are used to remediate toxic soils and wastewater (Singh et al. 2020).

## 7.2 Current Status of Water Pollution in India and World

Besides from the negative environmental, economic, and social consequences of insufficient water system and sanitization (Mara 2003; Johnson et al. 2008; Moore et al. 2003; Montgomery and Elimelech 2007), water is necessary for the asylum of children and the underprivileged (Theron and Cloete 2002). Waterborne sickness kills 10–20 million people each year, while nonfatal infection affects over 200 million individuals (Eshelby 2007; Leonard et al. 2003). Every day, 5000–6000 children die because of diarrhoea caused by polluted water (Hutton et al. 2007; Ashbolt 2004). Moreover, 0.78 billion of population lack access to safe drinking water worldwide (WHO 2013), resulting in serious health issues. Approximately, one billion people are expected to face shortfall of safe drinking water in the upcoming decades, and the present-day water supply will be cut by tierce.

The Central Pollution Control Board (CPCB), in 1995, declared 18 major rivers in India to be extremely polluted. Agricultural operations have an impact on water quality in general. Apart from a fast-declining groundwater table, the country is also dealing with groundwater contamination, which has afflicted 19 states, including Delhi. Fluoride poisoning has been found in over 150 districts across 17 states, with Rajasthan and Orissa bearing the brunt of the damage. A high fluoride concentration in drinkable water causes fluorosis, which results in brittle teeth, bones, and anaemia. The Gangetic delta groundwater is found to consist arsenic (toxin and carcinogen), putting the health of 35–70 million people in Bihar, West Bengal, and Bangladesh in danger. The cost of eradicating industrial water pollution, according to Murty and Kumar (2002), is around 2.5% of India's industrial GDP. According to Parikh (2004), the cost of avoidance is much lesser compared to the cost of harm. As per the Gallup poll, drinking water pollution is the most severe environmental concern in the US (Saad 2009). Increased salt loads entering surface water is another long-term issue as a result of road salt and excessive irrigation (Kaushal et al. 2005). In numerous coastal locations, such as India and China, overutilization of aquifers and increasing sea levels have exacerbated marine salt invasion into groundwater (Post 2005).

### 7.2.1 Toxic Contaminants in the Wastewater, Their Sources and Effects

Water is said to be "the lifeblood of the biosphere." Water can dissolve a variety of organic and inorganic chemicals, and toxins in environment, because it is a universal solvent. Pesticides, dissolved solids, viruses, and heavy metals damage water supplies, posing a serious hazard to plant, animal, and human health (Rezania et al. 2016). The most frequent dissolved solids in natural water are bicarbonates, phosphates, carbonates, sulphates, chlorides, and nitrates of potassium, sodium, calcium, and magnesium with traces of manganese, iron, and other minerals.

### 7.2.2 Heavy Metals

Toxicity of the heavy metals is a major problem across the whole world in recent years, as they have negative impacts on every type of biological things in an ecosystem. Progress in industries and agriculture, as well as rising population density; have further complicated the situation (Giguere et al. 2004). Toxic heavy metals biomagnified via the food chain, posing serious health risks to people and other living things (Madhav et al. 2020). Biomolecules' structure and biological functions are altered by heavy metal (McCormick et al. 2005). Non-degradable natural components of the earth's crust, these heavy metals, are toxic and lethal when they are not generated and digested by the body and accumulate in sensitive tissue (Ahamad et al. 2020). Heavy metal toxicity can also be biologically remediated by over expressing the metal binding proteins such as T4MBP (top 4 metal-binding protein) and HMP3 (human mettalothionein 3) in *E. coli* and were transformed into biobeads reducing copper, cadmium, and zinc concentration in wastewater by 87.2%, 27.3%, and 32.8%, respectively (Gupta et al. 2019).

### 7.2.3 Pesticides

Pesticides are extensively used into modern agriculture, essentially for increasing crop output and reducing post-harvest losses. Pesticide levels have been found at alarming amounts in India’s water, air, and soil, as well as biological materials and food (Viswanathan 1985). A few pesticides have been found to be deadly, cancer-causing, mutagenic, and carcinogenic (Deflora et al. 1993; Rehana et al. 1995). Pesticides were used 43,580 metric tonnes (MT) in 2001–2002. In India, technical grade chlorpyriphos was used at a rate of 5000 MT in 2002–2003. Singhal (2003). According to a WHO research, roughly 3% of agriculture workers in developing countries are poisoned every year, resulting in about 25 million cases of occupational poisoning (Jeyaratnam 1990).

### 7.2.4 Various Sources of Wastewater

There are numerous forms of wastewater depending on the source from which it is generated, some of which are described below:

- Dairy waste water
- Sewage Sludge
- Textile waste water
- Tannery waste water
- Pharmaceuticals waste water
- Carpet mill waste water
- Food waste water
- Slaughter House waste water
- Paper Industry waste water
- Phenolic waste water
- Domestic Waste water
- Beverage waste water
- Palm Oil Mill waste water
- Wine Industries waste water

Chemical, bacterial, and other unwanted components make up the majority of wastewater, which varies depending on where it comes from. Industrial discharge contains a huge number of hazardous chemicals and heavy metals such as zinc, cadmium, copper, nickel, lead, arsenic, mercury, antimony, and others due to the reduced biological content (Kong et al. 2010).

Agricultural wastewater consists of elevated concentration of chemicals (pesticides, weedicides, fertilizers, and so on) as well as biological material (algae, fungi, bacteria, and so on) (Reungsang et al. 2016). Organic substances account for 70% of wastewater, while inorganic compounds and a variety of gases account for 30%. Hydrogen sulphide, methane, oxygen, ammonia, carbon dioxide, and nitrogen are all common dissolved gases in wastewater (Li et al. 2013).

## 7.3 Sustainable Approach

Water, an important natural resource, is a life-sustaining essential. Water pollution from natural and man-made sources is increasing at an alarming rate, posing a huge risk to all living organisms across the globe, including different ecosystems. Over these years, researchers had tested as well as analysed several detoxification procedures and processes in order to lessen and address the current challenges (Kumar and Shahi 2018).

Water recovery treatment methods include advanced adsorption, oxidation, membrane bioreactors, chemical treatment, neutralization of acid and base in effluent, and incineration, to name a few (Jayaswal et al. 2018). Unfortunately, traditional and physical techniques have a number of significant drawbacks, including slow progress, high prices, secondary intermediate creation, and inefficient contaminant removal from the environment (Singh et al. 2017).

Bioremediation, often known as "natural purifier," is a method of cleaning contaminated environments with biological agents. In such cases, Ahmed and Fakhruddin (2018) is an acceptable technique or solution over traditional methods. Furthermore, because the by-products produced are not much harmful than the indigenous pollutants, bioremediation is the most promising biotechnology method (Abatenh et al. 2017a, b). Several mechanisms are engaged in the technical side of bioremediation (Arora 2018).

Techniques that use microorganisms or plants to help immobilize toxins and remediate water and soil include biosequestration, biodegradation, phytohydraulics, biological extraction, and volatilization. Since then, scientists have been studying the potential of microbes, such as bacteria, synthetic microbes, fungi, algae, to neutralize the aquatic and soil environment for bioremediation (Alegbeleye et al. 2017).

According to Dangi et al. enzymes are created by bacteria and play a crucial part in metabolic events (2019). Microbial bioremediation is more enticing since microbes will extensively attack, remove, and transform pollutants. Despite the promising results, bioremediation falls short due to biological and environmental variables (Rv 2016; Abatenh 2017b; Zhu et al. 2017). Environmental variables like pH, pressure, temperature, and nutrition source influences the pace of bioremediation (Xue et al. 2015). Bioremediation is also limited by the systems' bioavailability, bioactivity, and biochemistry (Zubairu et al. 2018).

### 7.3.1 Bioremediation Process

The manipulation of living systems to bring about desired chemical and physical changes in a restricted and regulated matter is known as bioremediation. (Singh and Ward 2004)

The term “bioremediation” is frequently used to characterise a wide range of microbial processes that occur naturally in ecosystems, including mineralization, detoxification, co-metabolism, and activation (Rochelle et al. 1989)

Bioremediation is one of the most promising strategies due to its safety, economic, and environmental features, also organic contaminants are transformed and even fully mineralized through this technique (Saval 2003). Bioremediation entails not only identifying the microorganisms that degrade the target molecule, but also the mechanisms and pathways of degradation at both the molecular and physiological levels (Ghosh et al. 2005) (Fig. 7.1).

The detoxification process targets hazardous chemicals by modifying, mineralizing, or converting them (Shannon and Unterman 1993). Bioremediation works by promoting the establishment of microbial consortia or microflora that are native to the polluted area and fulfil certain tasks (Agarwal 1998). Providing nutrients to stimulate development, adding an end electron receiver, and temperature regulations well as moisture content are all examples of how microbial consortia can be formed (Hess et al. 1997; Smith et al. 1998; Agarwal 1998). It has also been proven that adding similar strains of microbes to the nutritional medium improves the native microbial population’s ability to break down contaminants. Bioremediators are microorganisms that take part in bioremediation (Maheshwari et al. 2014).

### 7.3.2 Factors Influencing Microbial Remediation

A number of biotic and abiotic stimuli regulate microbial cell behaviour and proliferation, which has an impact on a broad range of biological activities of microbe community. The bioremediation process takes place in a multiphasic heterogeneous

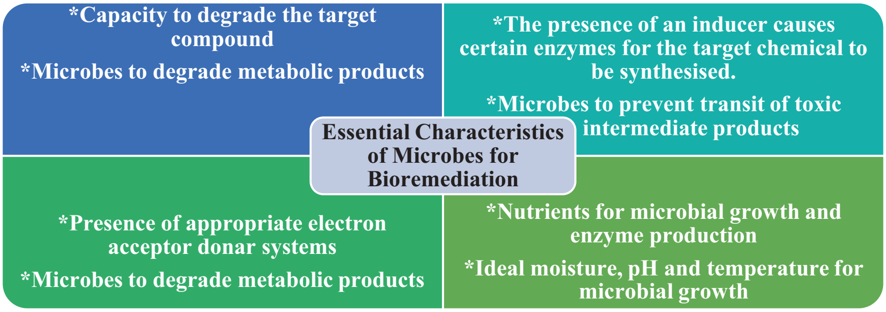

**Fig. 7.1** Some important features of microbes for Bioremediation

environment, which influences the rate of reactions (Boopathy 2000). The efficacy of a process diminishes when there is a lack of information about the elements that drive it (Lovely 2003). Microbes are excellent at adapting to new settings, but they are constrained in a number of ways. An immense understanding of microbial ecology is needed to improve microbiological action and anticipate the efficient process of bioremediation (Watanabe 2001).

Physicochemical or abiotic environmental attributes, biological or biotic variables and climatic conditions influence microbial processes, with climatic and physico-chemical conditions being amongst the important constituent influencing microbe metabolic activity.

### *7.3.3 Physicochemical Variables*

Physicochemical parameters include ionic strength, redox potential (Eh), solubility, pH, the absence or presence of electron donors and acceptors, temperature, as well as the age of organo-metallic ions.

The process of biosorption, whereby the pH of a solution alters the net negative charge on a microbial cell surface, is the first stage in the removal of toxic metals by bacteria. As a result of this transition, the ionic states of ligands such as amino acid groups, carboxyl residues, S–H groups, and phosphoryl residues changes (Sag et al. 1995). Bio-remediation approaches require microorganisms to reduce metal ions from high to low oxidation levels, whereas enzymes can only convert soluble metal ions to insoluble form (pH dependant). Typically, metals are soluble when they possess greater oxidation state (Garbisu and Alkorta 2003).

Solvability is crucial factor in OC breakdown because sparingly soluble or hydrophobic chemicals linger in the nature for indefinite time but are biologically unavailable (Pieper and Reineke 2000a, b). Metal ion solubility is affected by pH that rises as the pH of the medium falls, disrupts microbial cell adhesion (Blázquez et al. 2008). Metal ions must also cling to the microbial cell surface at lower pH values, whereas metal ions prefer to precipitate in an alkaline solution (Han and Gu 2010; Rajendran et al. 2002). *Pseudomonas* sp. and *Burkholderia cepacia* form gluconic acid, whereas *Rhizobium* sp. and *Bacillus firmus* makes ketogluconic acid, that lowers the solution's pH, also enhancing metal ion solvability (Robles-Gonzalez et al. 2008).

Organometallic compounds help for the mobilization of ions of the metal (Puzon et al. 2005). Toxic metal ions serve as a respiratory inhibitor in bacteria (such as $Zn_2$) and slows bioremediation dramatically (Beard et al. 1995). Biodegradation is aided by electron acceptors such as $SO_4$, $NO_3$, and Fe(III) oxides in anaerobic microbes and oxygen in aerobic microorganisms (Lovely 2003).

### *7.3.4 Biotic Factors*

Although biotic components have not been always visible, their significance is usually exposed when bioremediation techniques are used. Microbes have a number of inherent characteristics that influence substrate degradation, such as substrate specificity and encoding specific enzymes (proteins) is regulated by plasmid encoded genes, but in nature, microbes, particularly bacterial cells, have been observed to have varying substrate specificity (Mars et al. 1997). A positive bacterial function that aids in the breakdown of chemical compounds that are difficult to break down is “chemotaxis” (Pandey and Jain 2002).

Organohalide respiratory bacteria are difficult to separate and culture since they can only survive in groups. It is a function of community genomics or metagenomics, in which metagenomic sequencing offers data from member of the species of consortia that enable substrate depletion (Maphosa et al. 2010). Furthermore, the minimal conditions for survival of bacteria alter on a regular basis (Ingham et al. 2007). Microbes and microbial communities are critical to the normal functioning of Earth’s ecosystems, and changes in their metabolism, composition, or abundance can cause ecosystems to become unstable (Nweke et al. 2007).

### *7.3.5 Climatic Conditions*

Change in global climatic conditions is characterized by factors such as growing $CO_2$ levels and air temperatures. Microbes have a stronger ability to break down soil organic matter as $CO_2$ levels rise, and nutrients play an important part in carbon (C) cycling in ecosystems dominated by biotic and abiotic processes (Nie et al. 2013). According to studies on soil bacteria and climate change, changes in the physico-chemical activities of the microbial niche might affect microbial assimilation activity and hence the bio-remediation process (Sowerby et al. 2005; Castro et al. 2010; Nie et al. 2013). Climate, as well as microbial activity and soil physicochemical parameters, influence microbial extracellular enzyme production (Sowerby et al. 2005).

Frey et al. (2013) discovered better refractory substrate utilization efficiency by bacteria in soils at higher temperatures as a positive climate feedback, despite the fact that microbial populations are assumed to be limiting ecosystem-to-climate feedbacks (Bardgett et al. 2008). Increased $CO_2$ levels in the environment have been associated to increased bacterial abundance and decreased fungal abundance (Castro et al. 2010; Frey et al. 2008).

## 7.4 Types of Bioremediation

### 7.4.1 *Biostimulation*

The soil or ground water of a region is enriched with specific nutrients to increase the efficiency of native microbes. It focuses on fostering the growth of bacterial and fungal communities that are native or already exist. Fertilizers, growth supplements, and trace minerals are provided to begin with. Second, they can increase their metabolic rate and pathway by adapting to new environmental variables like temperature, pH, and oxygen (Kumar et al. 2011; Adams et al. 2015). A fraction of contamination may also serve as a stimulant, causing bioremediation enzyme operons to activate. The majority of the time, this important channel is kept open by providing food and oxygen to native bacteria. These nutrients are the basis of life, allowing bacteria for making things like energy, cell biomass, and pollution-degrading enzymes. They'll all need phosphate, carbon, and nitrogen to grow (Madhavi and Mohini 2012).

### 7.4.2 *Bioattenuation*

The process of removing pollutant concentrations from the environment is known as bioattenuation. The word "natural attenuation" encompasses terms such as "biotransformation" and "intrinsic remediation" (Mulligana and Yong 2004). When chemicals pollute the environment; environment employs four approaches to clear it up (Li et al. 2010). (a) The chemical substances are ingested via soil and groundwater bacteria and little bugs that live there. The chemicals can be transformed to innocuous gases and water once they have been thoroughly digested. (b) Chemicals have the ability to attach and bind to soil, allowing them to stay put.

### 7.4.3 *Bioaugmentation*

Bioaugmentation is a technique for increasing the biodegradative capability of local microbial populations by introducing pollutant-degrading microorganisms (native, foreign, or artificial) into a contaminated area. To help natural microbial communities, which preferentially feed on polluted sites, develop more quickly and effectively. Separated microbes of the clean-up area are maintained separately, bioengineered, and then reintroduced. When chloromethane, like tri and tetrachloroethylene, damage soil as well as groundwater, all important microorganisms are identified. It's used to make sure that microorganisms in the field can totally eliminate these poisons and convert them to non-toxic ethylene and chloride (Niu et al. 2009). The process of introducing engineered microbes into a system that operates as bioremediators, allowing complicated poisons to be eliminated quickly and fully, is known as bioaugmentation.

### *7.4.4 Bioventing*

Bioventing is the process of supplying oxygen to previously existing soil microorganisms in order to enhance the growth of naturally occurring or imported bacteria and fungi in the soil. It can also be seen in chemicals that break down when exposed to oxygen. Bioventing utilizes moderate flow rate of air to supply just ample oxygen for sustainment of microbial processes (Agarry and Latinwo 2015; Lee et al. 2006).

### *7.4.5 Biopiles*

Top soil that has been contaminated by aerobic endurance fixable hydrocarbons is serves in "biopiles." During the biodegradation process, biopiles (also known as bioheaps, biocells, compost Piles and biomounds) have been employed to minimize petroleum pollutant amount in top soils. A pump and piping system which either pushes air into the pile under high pressure or drag air through the pile under pressure gradient supplies air to biopile system (Delille et al. 2008). Microbial respiration enhanced microbial activity, causing adsorbed petroleum pollutants to break down quickly (Emami et al. 2012).

## 7.5 Advantages of Bioremediation

- The public supports bioremediation as an effluent processing method for polluted materials like soil since it is a natural occurring phenomenon. When a pollutant is present, the number of bacteria capable of digesting it increases; when the pollutant is eliminated, the biodegradative population decreases. Carbon dioxide, water, and cell biomass are examples of normally innocuous treatment by-products.
- Bioremediation does have the potential to remove a wide spectrum of contaminants completely. Many legally listed hazardous compounds can be transformed into non-hazardous equivalents.
- Instead of shifting toxins through one environmental medium to the other, such as from land to water or air, target contaminants can be completely eradicated.
- Bioremediation on-site is frequently possible without causing significant disruption to normal operations.

Bioremediation has potential to be less expensive than other hazardous waste removal methods since it eliminates the need to carry huge amounts of garbage off-site and the associated health and environmental risks.

## 7.6 Disadvantages of Bioremediation

- In bioremediation, only biodegradable chemicals can be employed. In a short amount of time, not all chemicals can be entirely eradicated. Some people are concerned that biodegradation products would stay longer or be more harmful than the parent compound.
- Biological processes are generally divided into sub-processes. Important site considerations include the existence of metabolically capable microbial populations, appropriate environmental growing conditions, and acceptable nutrient and contaminant concentrations.
- It might be difficult to extrapolate findings from laboratory and pilot-scale investigations to full-scale field operations.
- More study is needed on bioremediation systems that are suitable for locations with complex combinations of contaminants that are not equally disseminated in the environment. Bioremediation takes significantly longer than alternative treatment processes such as excavation and soil removal, or cremation, because contaminants can be solids, liquids, or gases.

Adequate quality measures for bioremediation remains a stumbling block for regulators. There is globally no recognized concept of “clean,” it is impossible to evaluate bio-remediation efficacy, and there is no acceptable bioremediation outcomes.

## 7.7 Remediation of Wastewater

Bioremediation is a field of biotechnology that involves using living organisms like microbes and bacteria to clear the contaminants and toxins of soil, water as well as other environments. Bioremediation is a process for cleaning up polluted groundwater or environmental difficulties like oil spills. Bioremediation promotes the growth of the microorganisms those consume pollutants like oil, solvents, and insecticides for foodstuff and energy. These bacteria converted pollutants, as well as innocuous gases like carbon dioxide, into small amounts of water. Bioremediation requires the right temperature, nutrition, and food. The scarcity of these components may cause pollution to take longer to clean up (Singh et al. 2020).

By introducing “legislative changes” to the surroundings, like molasses, vegetable oil, or just plain air, bioremediation circumstances can be enhanced. These modifications make it easier for bacteria to thrive, speeding up the bioremediation process.

### 7.7.1 Phycoremediation

Phytoremediation is the process of using macro- or microalgae to reduce or biotransform contaminants from wastewater, such as nutrients and harmful compounds (Mulbry et al. 2008; Olguin 2003). In microalgae production, algae are used for source of food, fuel, stabilizing agent, manure, compound, wastewater treatment, and power plants to reduce $CO_2$ emissions. A substantial quantity of organic matter and energy is produced by algae. Certain algal genera store up to 60% of their entire biomass as intracellular lipid, enhancing their energy value and biomass's heat of combustion (Gaikwad et al. 2016).

This method can help minimize cultivation costs while also helping to sequester carbon dioxide. Microalgae culture method selection is critical for maximizing microalgal productivity while staying within budget. The three types of microalgae cultivation are heterotrophic, photo-autotrophic and mixotrophic (Wang et al. 2013). According to various research, heterotrophic and mixotrophic development generates higher biomass and lipid content in many microalgae species than photoautotrophic cultivation (Chojnacka and Andrzej 2004; Vonshak et al. 2000; Chojnacka and Facundo 2004).

### 7.7.2 Mycoremediation

Mycoremediation has a potential to be a successful, economical, and eco-friendly acceptable solution for the ever-rising difficulty of soil and water contamination. Due to their vigorous growth, fungi are a suitable candidate for the clean-up of many contaminants, production of versatile extracellular ligninolytic enzymes, adaptability to fluctuating pH and temperature, vast hyphal network, high surface area to volume ratio, resistance to heavy metals, and presence of metal-binding proteins (Khan et al. 2019; Singh et al. 2015). It may be used to clean up various toxins produced by different enterprises, like herbicides, dyes, and pharmaceutical drugs, in real time. Therefore, an alternative, it can be used in bioreactors. Bioreactors are physicochemically regulated devices that aim to boost microorganism development (Aragão et al. 2020). Controlled metabolite utilization in the bioreactor and fungal biomass that is under control can be employed to speed up pollutant degradation (Tekere et al. 2019). So far, bioreactors have been built to treat effluent from the sugar and pharmaceutical industries. These bioreactors can also be utilized to remediate soil from herbicides, polycyclic aromatic hydrocarbons, insecticides, chlorinated solvents, tars, and explosives in situ (Tekere et al. 2019).

### 7.7.3 Mechanism Involved in Microbial Remediation

A group of microorganisms capable of digesting or altering harmful pollutants is referred to as a "microbial consortium." According to several studies, the following bacteria are particularly effective in this regard. Prokaryotic bacterial species such as *Flavobacterium*, *Geobacter*, *Pseudomonas*, *Actinobacter*, *Berijerinckia*, *Acaligenes*, *Methylosinus*, *Arthrobacter*, *Mycococcus*, *Xanthofacter*, *Nitrosomonas*, *Serratia*, *Nocardia*, *Exiguobacterium*, and *Mycobacterium* have shown efficacy in pollution breakdown. *Pleurotusos trateus*, *Aspergillus niger*, *Ganoderma lucidium*, *Penicillium*, *Phanerochaete*, *Rhizoctonia*, *Polyporus*, and other laccase-producing enzymes are eukaryotic fungus species that have been tested with a variety of environmental pollutants. Algal species such as *Chlorella vulgaris*, *Rhizoclonium hieroglyphicum*, and mixed algae culture (*Lyngbya* sp., *Microspora* sp., *Navicula* sp., *Spirogyra* sp., *Cladophora* sp., and *Rhizoclonium* sp.) are also known to show effective wastewater treatment. Algae including *Anabaena inaequalis*, *Stigeoclonium tenue*, *Chlorella* sp., *Synechococcus* sp., and *Westiellopsis prolifica* have evolved heavy metal resistance and hence have been used for its efficacy to remove heavy metals in wastewater (Bajguz 2011; Rahman et al. 2011).

Biosorption and bioaccumulation are the two main techniques of micro-bioremediation. Biosorption is a reversible and fast passive adsorption process. Biosorption requires a low cost because biomass can be obtained from industrial pollutants and regenerated in many cycles. In the bioremediation process, biosorption can use either alive or dead organic matter; however, bioaccumulation uses only living organic matter which will not be replenished, necessitating significant costs (Coelho et al. 2015). Unlike previous physicochemical treatments, another strategy depended on bacteria's metabolic ability to convert pollutants into simple, non-toxic molecules (Perpetuo et al. 2011).

Figure 7.2 summarizes the main types of microorganisms utilized for metal bioremediation, including bacteria, micro-algae, fungus, yeast, and the bioremediation techniques as well.

### 7.7.4 Bacterial Remediation

According to a study, heavy metal cations adsorb to the cellular walls of Gram-positive bacteria (Doyle et al. 1980). Several bacteria, including Azotobacter, Actinomycetes, and Pseudomonas, have been discovered to produce a variety of compounds that trap $Fe^{2+}$, which they need for the metabolic as well as biosorption activities (Pattus and Abdallah 2000). Jayashree et al. (2012) utilized *Pseudomonas* as a fuel-eating bacterium that can degrade hydrocarbons. *Pseudomonas syringae* also showed the creation of a link, that's required for the accumulation of cadmium, calcium, magnesium, zinc, copper, and mercury.

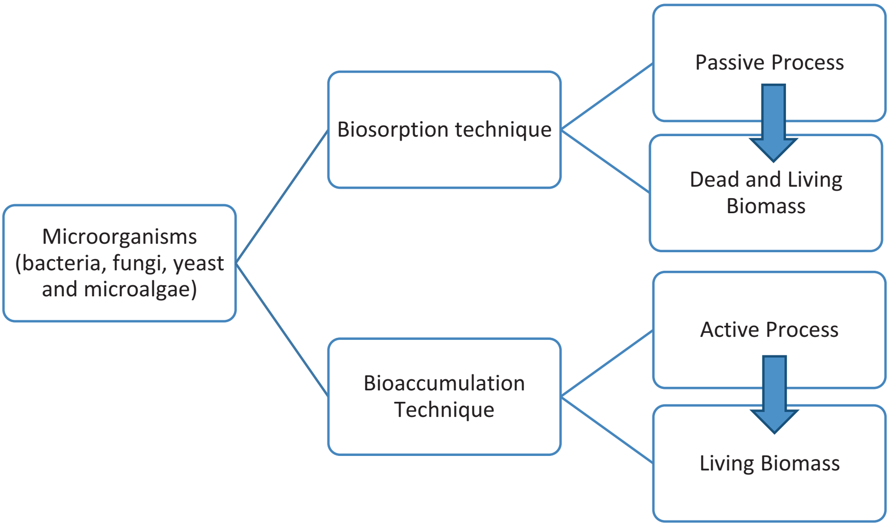

**Fig. 7.2** Methods used in Bioremediation

From coastal sediments, Bhakta et al. (2014) identified and reported 40 different type of cadmium (Cd) and arsenic (As)-resistant bacterial isolates. *Geobacter metallireducens* is a Fe(III) reducing bacteria capable of oxidizing benzene and naphthalene, as well as removing or reducing a radioactive waste, uranium from mining effluents and polluted groundwater (Lovely 2002). When given pure chemicals as a single source of life, *Exiguobacterium aurantiacum* has showed the ability to break down phenol and PAHs in batch culture at the laboratory (Jeswani and Mukherji 2012). COD and TOC were removed as a result of the activated sludge consortium and batch culture forming a good biofilm (RBC) on the spinning discs of a Rotating Biological Contractor (Mukherji and Jeswani 2011). Heavy metals can be absorbed by microorganisms from polluted water (Babel and Kurniawan 2003).

### *7.7.5 Genetic Engineering's Role in Bacterial Bioremediation*

The use of bio-engineering to create microbes that can digest poisons and pollutants is causing quite a stir right now. In hazardous waste and hydrocarbon bioremediation, the genetically altered bacteria showed to be more effective (Das and Chandran 2011). Bacteria have a tremendous metabolic diversity due to the inclusion of additional genes. To be successful in bioremediation, genetically modified bacterial methods require the change of catalysts as well as some metabolic processes (Pieper and Reineke 2000a, b). Using genetically modified fungi, algae, and bacteria, heavy metals were removed from hazardous waste. Chen and Wilson (1997) investigated the $Hg^{2+}$ accumulation selectivity of genetically modified *Escherichia coli* cells.

The findings revealed that the genetically engineered *Escherichia coli* cells effectively accumulated $Hg^{2+}$ in culture at small concentrations (0–20 M) over the pH ranges (3–11).

### 7.7.6 Fungi Remediation

The use of fungus to biodegrade poisonous and harmful compounds in the environment is known as fungal bioremediation. This is accomplished by increasing the activity of enzymes that transform harmful chemicals into non-toxic ones. Heavy metals can be gathered, absorbed, and concentrated in the mycelia of some fungus. In the mycoremediation of pollutants from the environment, yeast, microfungi, and higher fungi are used in soil and aquatic environments. The first step in achieving efficient mycoremediation would be to select the right fungus species for a given contaminant.

*Polyporus* sp. and *Phanaerochaete chrysosporium* (white rot fungus) are better bioremediation alternatives because they have a high potential for destroying a broad spectrum of enduring or noxious environmental pollutants like petroleum hydrocarbons, explosives, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and others (Wu and Yu 2007).

Through an ion exchange mechanism, the fungus *Aspergillus niger* and *Ganoderma lucidum* are employed to biosorb chromium (Ahluwalia and Goyal 2006; Muraleedharan and Venkobachar 1990).

### 7.7.7 Algal Remediation

Phycoremediation, also known as algal bioremediation, is the process of eliminating contaminants from the environment or converting them to a harmless form using algae. Phycoremediation is the utilization of microscopic or macroscopic algae to degrade as well as biotransform various contaminants, such as mineral and xenobiotics of polluted water and $CO_2$ of the atmosphere, in a broader sense. Algae are highly adaptable organisms that may thrive in a variety of environments, growing autotrophically, heterotrophically, or mixotrophically.

Algae perform an important role in reducing ion concentrations in aquatic bodies such as lakes and oceans in natural settings. They break down or absorb hazardous heavy ions and organic pollutants from the environment, like phenol compounds, hydrocarbons, pesticides, and biphenyls, leading to higher quantities into themselves than in the surrounding water (Shamsuddoha et al. 2006).

### *7.7.8 Wastewater Treatment by Alga*

Algae are important for acidity adjustment, sludge clean-up, and TD minimization, while standard approach needs multiple processes or phases. Temperature, light, salinity, and nutritional composition all have an impact on blue green algae, also known as cyanobacteria.

The biodiesel feedstock biomass, lipids, and fatty acids of microalgae *Scenedesmus obliquus* and *Micractinium reisseri* obtained through city effluent combined with rural runoff were examined by Abou-shanab et al. (2014). As per the study, *Micractinium reisseri*, a green microalga with a high biomass output, was shown to thrive in metropolitan effluent secondary and tertiary contaminants. The algae also assimilated nitrogen and phosphate efficiently, implying that this alga could be a suitable alternative for creating oil and biofuel from wastewater, according to the study. El-Sheekh et al. (2016) reduced hazardous contaminants in sewage, seawater, and well water samples utilizing the fresh-water alga *Chlorella vulgaris* and the coastal alga *Chlorella salina*.

## 7.8 Nanotechnology Involved in Wastewater Treatment

Nanotechnology, in its modern and postmodern forms, is a relatively new domain of science, although humans have been using it experimentally for centuries (Pradeep 2007; Anuradha 2013). It is a broad category that refers to a broad variety of techniques, involving microscopic procedures and systems (Abbasi et al. 2009). The promise of nanotechnology is thought to focus around 4444 nanoparticles. Nanoparticles' fundamental adaptability comes from the fact that they have distinct features from their bodies. Engineering materials are nanoparticles or nanomaterials with a size of between 1 and 100 nm in at least one dimension.

### *7.8.1 Nanobioremediation*

Nanobiotechnology has recently contributed significantly to the conversion of contaminants in soil, water, and air into ecologically favourable molecules. Combining standard bioremediation methods with nanobiotechnology or direct nano-remediation technology, in other words, could be a viable solution for submerging toxins in the environment.

Ion oxides also have a low environmental impact, have a limited solubility, and do not cause secondary contamination. As adsorbents, they have been utilized to reclaim heavy metals from waste areas (Amin et al. 2014). Nanoparticles are gaining popularity in enzyme-mediated repair technology because they generate an inert, biocompatible environment that interferes with enzymes' natural characteristics while assisting in their biological activity (Ferreira et al. 2015).

### 7.8.2 Remediation Using Nanomaterials and Nanoparticles

In bioremediation of contaminated systems, a range of nanomaterials and nanoparticles have been successfully used to remove a variety of harmful toxins in a number of settings.

Table 7.1 includes the various types of nanomaterials that are more effective at degrading contaminants, as well as the organisms or biological systems employed in the study. Different nanomaterials' ability to alleviate pollution with the help of organisms has been studied.

### 7.8.3 Success Stories Related to Bioremediation

- The oil ship Exxon Valdez sank off the coast of Alaska in 1989, dumping over 11 million gallons of oil. At the same time, bioremediation was growing steadily as a viable oil-cleaning technology. Exxon Mobil Corporation (XOM) and the Environmental Protection Agency (EPA) began investigating into a variety of chemicals. The efficacy of bioremediation appeared to be promising in early tests. Between 1989 and 1990, about 100,000 lb of fertilizer were applied to the affected areas in over 2000 applications. The cleaning was considered complete in mid-1992, with the fertilizer having removed nearly all type of oil compounds.
- In Deepwater Horizon oil disaster of 2010, 3.19 million barrels of oil escaped off the coastal area of the Gulf in Mexico. Because of the efficacy and lower cost of bioremediation, two approaches were used to start cleaning up after the Deepwater Horizon oil catastrophe.

During bioaugmentation, a small number of oil-degrading microbes are introduced into the afflicted area. Biostimulation entails adding minerals into the atmosphere for boosting the development of oil-degrading microbes that are already there.

- An outbound empty oil tanker BW Maple clashed with an inbound loaded oil tanker Dawn Kanchipuram near the Kamarajar Port in Ennore, Tamil Nadu, on January 28, 2017, dumping 9.9 million gallons (37,000 $m^3$) of oil into the Bay of Bengal. It is becoming more difficult to clean up oil spills in the sea without hurting the marine ecosystem. The National Institute of Ocean Technique (NIOT) has established an environmentally acceptable crude oil bioremediation system using consortium of marine microorganisms wheat bran (WB) immobilized on agro-residue bacterial cells.
- Loktak Lake (Ramsar site) in Manipur has traditional Phumdis (floating islands). Sewer and agro-chemicals are discharged in this body of water. Aquatic plants perform important activities such as phytosanitation and bioremediation.

In June 2008, an unforeseen oil spill occurred due to a crude oil trunk line breakdown in the region of Gujarat (Western India). Large expanses of land were covered with crude oil. Because the area was uninhabited, crop damage was minimal. This

**Table 7.1** Nanoparticle-mediated contaminant removal and bio-based processing

| Nanomaterials | Microorganisms or biological system used | Chemical presentation | System used | Degraded pollutants and removal efficiency |
|---|---|---|---|---|
| Nanoparticles | *Sphingomonas* sp. | Nanoscale zero-valent iron Au, Mn, (nZVI), Ag, Ti | Wastewater | Diphenyl ether; chlorinated hydrocarbons, pathogens (For diphenyl ether its 67%; for chlorinated Hydrocarbons its >76.8%) |
| Nanocomposites | *Arthrobacter globiformis* D47 | Microorganism-immobilized nanocellulose composites | Water | Herbicide (diuron) (>90%) |
| Nanomembranes | A biological extract of *Cynomorium coccineum* L. | Thin film composite polyamide | Industrial Wastewater | Cyanide compounds (~20%) |
| Nanotubes | Enzyme organophosphate hydrolase–MWNT paper | Unzipped carbon nanotube (CNT), single-walled CNT, and multi-walled CNT | Soil and water | Organophosphates and heavy metals (~22%) |
| Nanocrystals | Organo-phosphorus hydrolase, which has been over expressed in bacteria, undergoes enzymatic degradation. | ZnS | Wasteewater | Acid orange 7 and *p*-nitrophenol (>80%) |
| Nanosponge | Two organo-clays (Dellite 67 G and Dellite 43 B) | Cyclodextrin-based, highly cross-linked polymers | Soil | Triclopyr (3,5,6-Trichloro-2-pyridinyloxyacetic acid) (92%) |
| Nanopowders | Soil microorganisms | Nanopowder of Iron-oxide | Water | Direct red 23 (Azo dye) (98%) |

trunk pipeline was used by the Gujarat Refinery in India's Baroda city to carry unprocessed petroleum from oil-producing areas towards the oil refinery. Oil industry reacted quickly, shutting down unprocessed petroleum pumping into the troubled trunk line. The oil company quickly walled off the leak site to stop the spread of crude oil. After digging 14,694 m$^3$ of oil-contaminated soil and transporting it to a secure bioremediation pit with HDPE, OTBL refilled the excavated site with good rich farm soil. After oil polluted soil was dumped in a safe bioremediation pit, Oilzapper (crude oil degrading bacterial consortia) was utilized to break down

TPH. Oilzapper is a bacterial consortium that decomposes crude oil and consists of four different types of bacteria that can digest different parts of TPH. Oilzapper was mass-produced before it was powdered. Using the KT Oilzapper and a customized nutrient solution, the oil-contaminated area was completely cleansed, and the soil was subsequently recovered and transformed to green cover.

## 7.9 Conclusion

Contamination of water is a serious worldwide problem, not a local one. Clean water will undoubtedly aid survival while posing less hazard to public health and the aquatic environment. As a result, it is critical to remove diesel hydrocarbons from water bodies, which are mostly aliphatic and aromatic components. Bioremediation is the possible way for reclaiming polluted water. High salinity bacteria may absolutely be employed to decompose several organic contaminants under high salinity or saline conditions.

One of the pollutants detected within acquiring water resources is improper or inadequately treated water discharge. Effluents such as algal blooms fertilizers, toxic metals, hydrocarbons, microbial pathogens, endocrine disruptors, and biomolecules can be deposited when wastewater discharged come into contact with receiving water bodies. The occurrence of such compounds in water affects marine life's eco-balance as well as puts human life at risk. Metal poisoning is one of them, as are other concerns. Metal toxicity, eutrophication, as well as other inflammation, as well as a range of water-borne illnesses, are only a few of the issues. Wastewater effluents should be processed before being released to protect ecosystems and public health. Some of the treatment alternatives for wastewater clean up include chemical remediation, phytoextraction, physical methods, and microbiological remediation approaches.

Despite their significance in wastewater remediation, these treatment technologies have constraints, however most wastewater treatment plants combine them in their remediation processes. Engineered microorganisms and procedures should be planned and incorporated from the research phase to the realistic and experimental level in order to make substantial improvements in the utilization of microorganisms in the biological treatment to clean ups. More refined operational methods, well-studied and created microbes are required to efficiently employ improved operational strategies, well-studied and developed microorganisms for the improvement of environmental restoration, circulation economy, and societal benefits. To construct stronger environmental management in the future, it is critical to bring together academics from many disciplines, as well as updated technologies and platforms.

## 7.10 Future Perspectives

Future studies could concentrate on metagenomics (community structure), microbial identification, and bioremediation in a variety of environments. Because urbanization is a global phenomenon, treating garbage with naturally occurring and bioengineered bacteria is not an affordable technique because that requires significant amount of infrastructure and money. Commercial waste treatment is currently feasible, but the cost of doing so outweighs the benefits. Scientists are constantly attempting to increase the microbial waste remediation's economic benefits. Waste-to-energy conversion via microbial activity, biofertilizer generation, and material recycling are just a few examples of environmentally beneficial waste-to-energy conversion.

Other study topics that have yet to be thoroughly examined include mechanistic approaches to degradation and elimination, microbial adaptation to altering surroundings resistant metabolites, the chemistry of new xenobiotic compounds and proteomics. Microbe adaptability makes determining the optimum pollution remediation strategy more challenging for researchers; as a result, more precise techniques for identifying microorganisms and substrate specificity are required. Microbial resistance to various organic substances develops as a result of bacteria exchanging genetic information, and the rate at which this information is transmitted may demand a scientific monitoring study to verify that the living world is free of the extensively resistant strains.

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# Chapter 8
# Phytoremediation and Phycoremediation: A Sustainable Solution for Wastewater Treatment

**P. P. Sameena, E. Janeeshma, Nair G. Sarath, and Jos T. Puthur**

**Abstract** Apart from food and shelter, clean water is an unavoidable pre-requisite for the existence of human life. However, the exponential growth of population and ever-increasing industries becomes a major threat to natural water sources. Currently, numerous conventional wastewater treatments are employed, but most of them are not effective as the complete elimination of the contaminants is impossible. In this context, phytoremediation and phycoremediation of wastewater are coming into focus. Aquatic plants and algae are excellent candidates for the removal of organic and inorganic contaminants from wastewater. These plants and algae have strong tolerance mechanisms towards toxic pollutants, bioaccumulation potential, and increased biomass production. They can absorb the toxic levels of domestic, agricultural, and industrial xenobiotics from the wastewater. Therefore, this chapter is a comprehensive approach for detailing wastewater remediation using aquatic plants and algae and biomass applications for bioenergy production.

**Keywords** Aquatic plants · Biochemical oxygen demand · Eutrophication · Industrial effluents · Macroalgae · Microalgae

## 8.1 Introduction

Clean water is an unavoidable necessity of all living organisms. The rapid population rise of humans and their uncontrolled exploitation of natural resources pollute the surface and ground waters. Human interferences result in the discharge of organic and inorganic toxic pollutants into the water sources and lead to the decline of freshwater on earth (Mustafa and Hayder 2021a). The industrial blooming in recent times is the cause for release of a huge amount of untreated water into the soil and water bodies (Sarath and Puthur 2020). The wastewater from the textiles and

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bleaching industries contains highly toxic pollutant stuff, including colouring agents and dyes. This uncontrolled release of pollutants declines the water quality by decreasing or increasing the mineral or other components (Ahila et al. 2021). Besides, the sewage waste exoneration into the water bodies comprising of a vast quantity of organic nutrients such as nitrogen (N), phosphorus (P), and potassium (K), causes eutrophication and affects the oxygen content in the water bodies, and disturbs the living diversity of aquatic organisms (Emparan et al. 2019). The over-accumulation of the organic components results in foaming, discoloration, and enhanced growth of toxic algal species (Driscoll et al. 2003). Besides the toxicant accumulation, the augmentation of salinity also declines the quality of drinking water, which is a serious problem nowadays (Sarath et al. 2021). The imbalance of the natural components of the water, in turn, affects the aquatic ecosystem and causes severe problems for other dependent ecosystems. The scarcity of freshwater has given much importance to the remediation of wastewater. Among them, sustainable means of remediation using biological methods have great attention due to their eco-friendly nature.

Conventionally various technologies were utilized for the removal of the organic and inorganic pollutants from the wastewaters. It includes ion exchange, reverse osmosis, adsorption, electrochemical treatments, and chemical precipitation (Bairagi and Ali 2020). However, these methods have some disadvantages, such as requirement for high input of energy, the release of carbon to the environment, the discharge of sludge, and high maintenance costs (Elbasiouny et al. 2021). Therefore, sustainable means of wastewater remediation using toxicant tolerant aquatic plants have much importance, and their eco-friendly and cost-effectiveness make this technique more unique than conventional techniques. The remediation of wastewater using tolerant aquatic plants is termed as phytoremediation. It is a broad term not only applicable in the case of aquatic plants but also for all the plants, including terrestrial (Sarath et al. 2020). The technology of remediation using different algal species (micro and macro) is termed phycoremediation. It is an important one because of the easy and fast growth of the algae in the water bodies (Shackira et al. 2021). The algae-mediated remediation or transformation of the toxic pollutant from the wastewaters and further utilization of these algal species has several applications in energy production. The high biomass and energy content makes it a more economical and sustainable solution for wastewaters (Ahmad et al. 2020). Phytoremediation utilizes various types of plants to remove the toxicant from wastewaters and it includes several mechanisms such as phytoextraction, rhizofiltration, phytodegradation, and phytovolatilization.

Extracting the pollutants from the wastewater and sequestrating in the plant body is the principal strategy involved in phytoextraction (Hejna et al. 2021). The remediation of wastewater using plants is already widely reported. The free-floating aquatic weed plants have been known to remove pollutants from the wastewaters. The weed characters such as speedy multiplication and vast growth rate favours its phytoremediation potential. *Eichhornia crassipes*, *Lemna* spp., *Pistia stratiotes*, *Limnobium laevigatum*, are reported to be potential for the decontamination of wastewaters (Sudiarto et al. 2019). This chapter discusses the eco-friendly and sustainable means of wastewater remediation. It includes the exploitation of the aquatic plants (phytoremediation) and algae (phycoremediation) for wastewater decontamination.

## 8.2 Potential Candidates Used for Wastewater Treatment

To safeguard our water resources from pollutants, we can use various biological remediation techniques or agents. It includes the aquatic plants and algal species. It has got multi-application of remediation and also for bioprospecting. The significant candidates commonly used for the remediation include tolerant aquatic plants, microalgae, macroalgae, and some pteridophytes. Recent studies related to wastewater treatment and phytoremediation of aquatic plants, pteridophytes, macro and microalgae are detailed in Table 8.1.

### *8.2.1 Aquatic Plants*

Recently researchers have reported the potential capability of aquatic plants to remove organic and inorganic pollutants from the water bodies. They are one of the necessary forms of the living system for cleaning up the water bodies, which can remediate the contaminants in the wastewater via phytodegradation, rhizoflitration, phytotransformation, phytoextraction, or phytovolatilization techniques (Anand et al. 2017). The plant species ideal for phytoremediation purposes must have a good root system, fast-growing and high biomass producing plants, and quickly grow in adverse environments (Ali et al. 2013). Various aquatic plants used for wastewater decontamination include *Scirpus*, *Phragmites*, *Typha*, *Lemna*, *Hydrilla*, *Eichhornia*, *Pistia*, *Phalaris*, and *Ipomoea*. Out of these, *Lemna minor* (duckweed) is one of the most effective macrophyte for wastewater treatment, with the potential to remediate organic pollutants, pharmaceuticals, agrochemicals, dyes, petroleum hydrocarbons, heavy metals, nanomaterials, radioactive wastes, and other related pollutants (Ekperusi et al. 2019).

Similar to the plants included in angiosperm groups, some pteridophytes, such as *Azolla*, *Salvinia*, and *Pteris*, are also utilized for the decontamination of wastewater. Sood et al. (2012) observed the potential of *Azolla* for the successful remediation of radionuclides, toxic metals, pesticides, dyes, and other organic contaminants from the aquatic ecosystem. The doubling of the biomass within 2–4 days and the free-floating nature of *Azolla* make it easy to harvest biomass, for the disposal and/or recovery of metal ions (Hanafy et al. 2020). Likewise, Mustafa and Hayder (2021b) studied the potential of *Salvinia molesta* for the tertiary treatment of wastewater. They reported that this plant could remove 82.6% of COD (chemical oxygen demand), 91% of BOD (biochemical oxygen demand), and 96.8% of the colour in the wastewaters within 14 days of treatment. These observations indicate the

**Table 8.1** Some of the recent studies related to wastewater treatment and phytoremediation of plants and algae in aquatic ecosystem

| Plant/algal species | Type of wastewater | Wastewater quality | Exposure time | Major outcome | References |
|---|---|---|---|---|---|
| Aquatic angiosperms | | | | | |
| *Carex cuprina* | Industrial effluents | Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sn, Zn, Phenanthrene, pyrene and anionic detergent LAS | 113 days | Enhanced tolerance and accumulation of organic and inorganic contaminants | Guittonny-Philippe et al. (2015) |
| *Centella asiatica* | Aquaculture wastewater | 45.67 ± 0.60 mg/L TSS;<br>4.20 ± 0.10 mg/L $NH_3$–N;<br>0.35 ± 0.10 mg/L $PO_4^{3-}$;<br>8.29 ± 0.02 pH; 205 ± 1.00 NTU Turbidity | 14 days | Removal of 98% of $NH_3$–N, 90% of TSS, and 64% of $PO_4^{3-}$ | Nizam et al. (2020) |
| *Eichhornia crassipes* | Aquaculture wastewater | 45.67 ± 0.60 mg/L TSS;<br>4.20 ± 0.10 mg/L $NH_3$–N;<br>0.35 ± 0.10 mg/L $PO_4^{3-}$;<br>8.29 ± 0.02 pH; 205 ± 1.00 NTU turbidity | 14 days | Removal of 98% of $PO_4^{3-}$, 96% of TSS, and 74% of $NH_3$–N | Nizam et al. (2020) |
| *Ipomoea aquatica* | Aquaculture wastewater | 45.67 ± 0.60 mg/L turbidity;<br>4.20 ± 0.10 mg/L $NH_3$–N;<br>0.35 ± 0.10 mg/L $PO_4^{3-}$;<br>8.29 ± 0.02 pH; 205 ± 1.00 NTU Turbidity | 14 days | Removal of 73% of TSS and $NH_3$–N, and 50% of $PO_4^{3-}$ | Nizam et al. (2020) |
| *Lemna minor* | Textile, distillery, and domestic wastewater | Textile, distillery and domestic wastewaters blended at 3:1:18 ratio | 28 days | Removal efficiency of 92% COD and BOD | Amare et al. (2018) |
| *Myriophyllum aquaticum* | Heavy metal contaminated water | Metals such as Ni, Pb and Zn (0.05–20 mg/L) | 7 days | Enhanced accumulation of Ni, Pb and Zn without any toxicity symptoms | Harguinteguy et al. (2015) |

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|---|---|---|---|---|---|
| *Pistia stratiotes* | Aquaculture wastewater | 45.67 ± 0.60 mg/L TSS;<br>4.20 ± 0.10 mg/L $NH_3$–N;<br>0.35 ± 0.10 mg/L $PO_4^{3-}$;<br>8.29 ± 0.02 pH; 205 ± 1.00 NTU turbidity | 14 days | Removal of 98% TSS, 78% of $NH_3$–N, and 89% of $PO_4^{3-}$ | Nizam et al. (2020) |
| *Scirpus grossus* | Pb contaminated wastewater | 50 mg/L Pb | 98 days | 99–100% Pb removal efficiency | Tangahu et al. (2013) |
| | Sago mill effluent wastewater | 937 ± 66 mg/L TSS;<br>8920 ± 256 mg/L COD;<br>965 ± 53 mg/L BOD | 80 days | Removal of 98%, 88% and 93% for TSS, COD, and BOD, respectively. | Nash et al. (2020) |
| Pteridophytes | | | | | |
| *Azolla filiculoides* | Textile, distillery, and domestic wastewater | Textile, distillery and domestic wastewaters blended at 3:1:18 ratio | 28 days | Removal efficiency of 96% COD and 90% BOD | Amare et al. (2018) |
| *Pteris vittata* | Artificially contaminated with tetracycline antibiotics | Tetracycline antibiotics about 1.0 mg/kg | 7 days | Complete removal of tetracycline antibiotics from the medium within 5 days of exposure | Li et al. (2015a) |
| *Salvinia molesta* | Aquaculture wastewater | 45.67 ± 0.60 mg/L TSS;<br>4.20 ± 0.10 mg/L $NH_3$–N;<br>0.35 ± 0.10 mg/L $PO_4^{3-}$;<br>8.29 ± 0.02 pH; 205 ± 1.00 NTU Turbidity | 14 days | Removal of 9.3% of TSS, 88.6% of $PO_4^{3-}$ and 63.9% of $NH_3$–N | Nizam et al. (2020) |
| Macroalgae | | | | | |
| *Cladophora* sp. | Industrial wastewater | 13.4% N, 1.4% P, pH of 9.7 ± 0.2 | 3 weeks | 11–16% ash content and enhanced biomass | Lawton et al. (2013) |

(continued)

**Table 8.1** (continued)

| Plant/algal species | Type of wastewater | Wastewater quality | Exposure time | Major outcome | References |
|---|---|---|---|---|---|
| *Gracilaria chouae* | Integrated multi-trophic aquaculture system | Eutrophication due to excess phosphorus and nitrogen | 47 days | Concentration of N decreased quickly from 0.971 to 0.570 mg/L and P from 0.052 to 0.028 mg/L | Wu et al. (2015) |
| *Gracilaria lemaneiformis* | Integrated multi-trophic aquaculture system | Eutrophication due to excess phosphorus and nitrogen | 35 days | Eutrophication index value decreased from 14.5 to 8.4 | Wei et al. (2017) |
| *Gracilaria tikvahiae* | Integrated multi-trophic aquaculture system | Eutrophication due to excess phosphorus and nitrogen | 18 days | Recovery of nearly 35% of the N input. | Samocha et al. (2015) |
| *Oedogonium* sp. | Industrial wastewater | 13.4% N, 1.4% P, pH of 9.7 ± 0.2 | 3 weeks | Productivity 8.0 g m$^2$/day, 3–8% ash content, 45% carbon content and 20 MJ/kg heating value | Lawton et al. (2013) |
| *Spirogyra* sp. | Industrial wastewater | 13.4% N, 1.4% P, pH of 9.7 ± 0.2 | 3 weeks | 12–19% ash content and enhanced biomass | Lawton et al. (2013) |
| *Ulva lactuca* | Wastewater from sludge-fed biogas plant | Enrichment of $NH_4^+$ (2043 mg/L), $NO_3^-$ (18 mg/L) and ortho-phosphate (484 mg/L) | 18 days | Nutrient removal rates of 22.7 mg N/g dw/day and 2.7 mg P/g dw/day, biomass with rich source of protein, and the content of heavy metals did not exceed limit values to use as animal feed or soil improvement | Sode et al. (2013) |
| *Chaetomorpha linum* | Municipal wastewater | 102.4–307.6 mg/L COD, 8.9–24.5 mg/L $NH_3$–N, 0–0.83 mg/L $NO_3$–N, 0.75–2.35 mg/L TP, 3.78–32.6 N/P ratio and pH 7.28–7.54 | 3 months | Biomass productivity of 10.7 ± 0.2 g AFDW/m$^2$/day, with removal efficiency of 86.8 ± 1.1% N and 92.6 ± 0.2% P | Ge and Champagne 2017 |
| Microalgae | | | | | |

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|---|---|---|---|---|---|
| *Chlorella* sp. | Wastewater after primary settling | 32.2 ± 0.4 mg/L $NH_3$–N,<br>6.86 ± 0.05 mg/L TP,<br>38.95 ± 1.91 mg/L TN,<br>224.0 ± 4.2 mg/L COD and 4.7 Inorganic N/P | 9 days | Growth rate of 0.429/day, with removal rate of 74.7% $NH_3$–N, 90.6% P, 56.5% COD | Wang et al. (2010) |
| *Coleastrum* sp. | Primary settled sewage water | COD 70 m $O_2$/L, BOD 15 m $O_2$/L, TSS 270 mg/L, TN 41 mg/L and TP 4.7 mg/L | 10 days | Growth rate 0.55 ± 0.01/day biomass productivity 157.2 ± 8 mg/L/day, lipid productivity 22.6 ± 1.5 mg/L/day and energy productivity 3.0 ± 0.4 kJ/L/day | Mehrabadi et al. (2017) |
| *Desmodesmus communis* | Urban wastewater effluents | N/P 30:1, 123 ± 22 mg/L TSS,<br>2.39 ± 0.67 mg/L $PO_4^{3-}$,<br>32.39 ± 1.05 mg/L $NH_3$–N,<br>68 ± 12 mg/L VSS | 14 days | 9.7 wt.% TFAs, 1.64 ± 0.02 g/L biomass, complete removal of $NH_3$–N | Samorì et al. (2014) |
| *Desmodesmus* sp. | Primary settled sewage water | COD 70 m $O_2$/L, BOD 15 m $O_2$/L, TSS 270 mg/L, TN 41 mg/L and TP 4.7 mg/L | 10 days | Growth rate 0.56 ± 0.03/day, biomass productivity 169.3 ± 17 mg/L/day, lipid productivity 36.6 ± 1.6 mg/L/day and energy productivity 3.3 ± 1.2 kJ/L/day | Mehrabadi et al. (2017) |
| *Micractinium pusillum* | Primary settled sewage water | COD 70 m $O_2$/L, BOD 15 m $O_2$/L, TSS 270 mg/L, TN 41 mg/L and TP 4.7 mg/L | 10 days | Growth rate 0.57 ± 0.02/day, biomass productivity 177.2 ± 11 mg/L/day, lipid productivity 43.2 ± 3.1 mg/L/day and energy productivity 3.9 ± 0.3 kJ/L/day | Mehrabadi et al. (2017) |
| *Mucidosphaerium pulchellum* | Primary settled sewage water | COD 70 m $O_2$/L, BOD 15 m $O_2$/L, TSS 270 mg/L, TN 41 mg/L and TP 4.7 mg/L | 10 days | Growth rate 0.59 ± 0.01/day, biomass productivity 188.9 ± 10 mg/L/day, lipid productivity 61.0 ± 2.3 mg/L/day and energy productivity 3.8 ± 0.6 kJ/L/day | Mehrabadi et al. (2017) |

(continued)

**Table 8.1** (continued)

| Plant/algal species | Type of wastewater | Wastewater quality | Exposure time | Major outcome | References |
|---|---|---|---|---|---|
| *Pediastrum boryanum* | Primary settled sewage water | COD 70 m $O_2$/L, BOD 15 m $O_2$/L, TSS 270 mg/L, TN 41 mg/L and TP 4.7 mg/L | 10 days | Growth rate 0.56 ± 0.02/day, biomass productivity 156.6 ± 20 mg/L/day, lipid productivity 34.6 ± 2.2 mg/L/day and energy productivity 3.1 ± 0.2 kJ/L/day | Mehrabadi et al. (2017) |
| *Scenedesmus* | Domestic wastewater | DOC 112 ± 0.9 mg/L, COD 235 ± 0.8 mg/L, TN 41 ± 0.8 mg/L, $NH_3$–N 32.7 ± 2.2 mg/L, TP 8.4 ± 0.3 mg/L, TSS 162 ± 8 mg/L | 21 days | 32.2% algal lipid content and 32 mg/L TAG production, with a removal efficiency of 97% TP and 90% TN | Zhang et al. (2014) |
| *Spirulina platensis* | Primary effluent | COD 255 ± 3 mg/L, $NH_3$–N 30.0 ± 0.5 mg/L, TP 10.0 ± 0.5 mg/L, C:N:P ratio of 2.6:3.9:1 | 28 days | Fast growth rate and efficient uptake of $CO_2$ along with a removal efficiency of 97.2 COD, 99.6% TIN and 99.41% TP | Almomani et al. (2019) |
| Microalgal-cyanobacterial consortium with dominance of *Scenedesmus* | Domestic wastewater | 3.2 g/L TSS, 76 ± 26 mg/L TOC, 152 ± 34 mg/L IC, 106 ± 9 mg/L TN, 93 ± 9 mg/L $NH_3$–N, 39 ± 12 mg/L $SO_4^{2-}$ and 33 ± 8 mg/L $PO_4^{3-}$ | 208 days | Removal efficiency of 85% $CO_2$, 100% $H_2S$ and effluent TSS concentrations 26 ± 12 mg TSS/L along with biomass concentration of 2047 ± 186 mg/L | García et al. (2017) |

*BOD*: Biochemical oxygen demand; *COD*: Chemical oxygen demand; *DOC*: Dissolved organic carbon; *IC*: Inorganic carbon;
*LAS*: Linear alkylbenzene sulfonate; *$NH_3$–N*: Ammoniacal nitrogen; *TAG*: triacylglycerol; *TFAs*: total fatty acids; *TIN*: Total inorganic nitrogen; *TN*: total nitrogen; *TOC*: Total organic carbon; *TP*: total phosphorus; *TSS*: Total suspended solids; VSS: Volatile suspended solids.

potential of pteridophyte species in wastewater remediation, and they help to restore the dissolved oxygen in the contaminated water.

### 8.2.2 Microalgae

The large-scale use of algal cultures to treat wastewater and biomass production was recognized 75 years ago. The principal algae used for this purpose were the species of *Chlorella* and *Dunaliella* (Abdel-Raouf et al. 2012). Microalgae can be implemented not only to remove toxic metals and pesticides but also to remove pharmaceutical compounds from industrial areas (Wang et al. 2017; Nie et al. 2020). Therefore, microalgae can be effectively utilized to treat diverse liquid effluents from agricultural and industrial areas. Moreover, the harvested biomass after bioremediation can be used to produce biofertilizers, fuels, fish and animal feed (Molazadeh et al. 2019).

The metal-binding proteins and other receptor molecules in the microalgal cell wall enable the binding of metal ions to the algae, termed as biosorption (Ubando et al. 2021). After successful biosorption, some microalgae can use the toxic compounds for the cellular metabolic processes, rendering them less toxic (Shackira et al. 2021). Singh et al. (2017) studied the phycoremediation potential of four microalgae such as *Parachlorella kessleri-I*, *Chlorella* sp., *Chlamydomonas reinhardti*, and *Nannochloropsis gaditana* in municipal wastewater. The results pointed out that all the studied four microalgae were potential candidates for the phycoremediation of wastewater, with the highest contaminant removal efficiency to the *P. kessleri-I* strain. This strain effectively removed 98% of phosphate along with a 50% increase in biomass and a 115% increase in lipid yield in 100% municipal wastewater (Singh et al. 2017). Therefore, *P. kessleri-I* strain can be successfully applied for the dual purpose of municipal wastewater treatment along with biodiesel production.

### 8.2.3 Macroalgae

Macroalgae, commonly called seaweeds, are fast-growing and used for ecosystem balancing to mitigate eutrophication in water bodies. They can grow in nutrient-rich water and clean it by accumulating toxic metals and other organic and inorganic contaminants (Silkina et al. 2017). Eutrophication results in the over-accumulation of inorganic nutrients such as nitrogen and phosphorus in the water bodies, which can be successfully utilized to efficiently grow economically important plants such as seaweeds. In addition, seaweeds can be utilized (1) as an adsorbent in wastewater treatment plants to replace the functional activated carbon, (2) for the production of phycocolloids, and (3) as a source of natural polymer utilized for the development of biodegradable plastics (Freile-Pelegrín et al. 2007; Chan and Matanjun 2017;

Arumugam et al. 2018). These multiple applications and contributions have increased the demand and cultivation of macroalgae.

As the majority of the wastewater streams and industries are situated near the freshwater systems, the treatments of these wastewaters require the algae which inhabit the freshwater ecosystems. The studies related to wastewater treatment by macroalgae have mainly focused on the removal of BOD, COD, heavy metals, phenols, and dyes. Lawton et al. (2013) studied diverse freshwater macroalgae to treat industrial wastewater. They observed that the species of *Cladophora*, *Oedogonium*, and *Spirogyra* are reliable candidates for the effective treatment of wastewater.

## 8.3 Role of Aquatic Plants and Algae in Wastewater Treatment

Algae and aquatic plants are autotrophs and can synthesize organic food from the inorganic nutrients and organics available in the waste materials. Decayed matter, plant nutrients, synthetic organic chemicals, inorganic chemicals, microplastics, sediments, radioactive substances, oil, antibiotics, pharmaceuticals, personal care products, surfactants, metal ions, and pesticides are the most common contaminants found in wastewater (Petrović et al. 2003; Vysokomornaya et al. 2015; Tran et al. 2018). Biodegradation, mineralization, utilization of C, N, and P sources, rhizofiltration, bioremediation are the different bioprocesses that aid to improve wastewater remediation by aquatic plants and algae. The major processes of wastewater treatment mediated by aquatic plants and algae are diagrammatically represented in Fig. 8.1.

Different waste materials have different degradation pathways and kinetics. The algal growth is achieved by the biodegradation of different components in the wastewater. One of the emerging contaminants the antibiotic tetracyclin was effectively degraded by algae *Chlorella vulgaris*, through biosorption property of these organisms. Moreover, the excess amount of tetracyclin did not cause any significant reduction in the algal biomass production (de Godos et al. 2012). These organisms also efficiently degraded another antibiotic, levofloxacin. The biodegradation of levofloxacin was significantly higher under saline wastewater (171 mM NaCl solution) by the efficient intracellular biodegradation and bioaccumulation potential of *Scenedesmus obliquus*. In this study, the role of biocatalysts released by *S. obliquus* involved in the biodegradation was also examined, and dehydroxylation, decarboxylation, side-chain breakdown, ring cleavage, and demethylation were found to be the different biochemical changes that augmented the degradation rate of the contaminant (Xiong et al. 2017). Like these algae, aquatic plants are also involved in biodegradation of waste material by the activity of different enzymes (Ma et al. 2020).

The improved biodegradation increases the dissociation of organic and inorganic components in the waste material, and this process of mineralization increases the

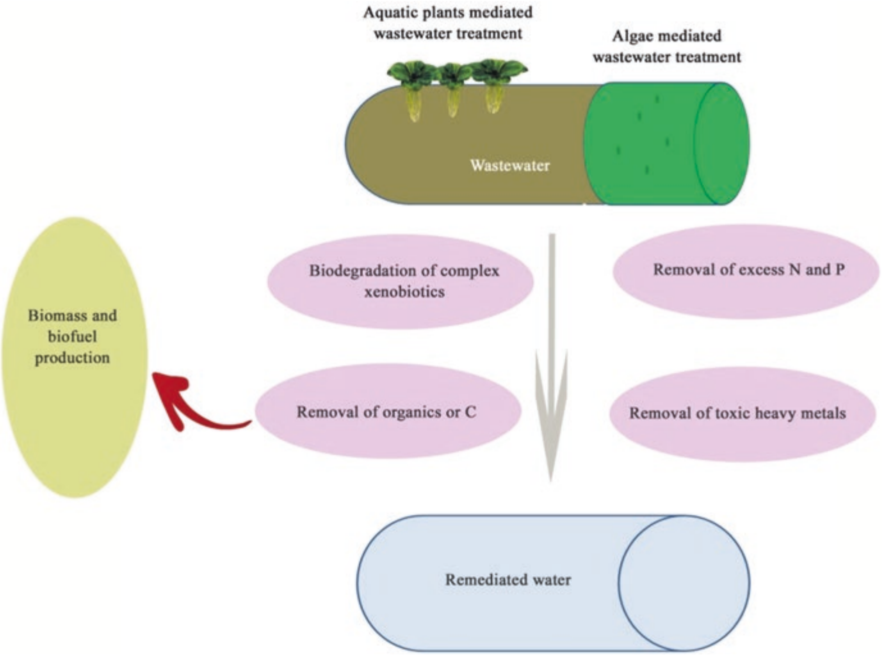

**Fig. 8.1** The diagrammatic representation of major processes involved in wastewater treatment mediated by aquatic plants and algae

content of different essential elements in wastewater. The release of N, P, K, Mg, Fe, C, H, and S to the wastewater aids to increase the assimilation of these minerals by plants and algae. This mineral acquisition potentially increases the growth and development of these organisms. Rhizofiltration and bioremediation are the two crucial processes for the removal of heavy metals from wastewater. These in situ technologies contribute significantly to the efficient working of wastewater treatment systems (Yadav et al. 2011). The filtration efficiency of the *Carex pendula* was exploited to remove the excess lead (Pb) content in the wastewater. Accumulation of Pb in the root biomass of the plants improved the removal kinetics of Pb (Yadav et al. 2011). This potential of plants like *C. pendula* can be very well utilized in the clearing of wastewater contaminated with other heavy metals.

Similarly, bioremediation potential of algae was also found to aid in the removal of toxic metals from the water. The biosorption and immobilization potential of these organisms helps to filter the heavy metals from the water (Kiran Marella et al. 2020). Different diatoms, blue-green, green, and brown algae, exhibited bioremediation properties (Kiran Marella et al. 2020). All these processes involved in wastewater remediation are detailed in the following sections.

### *8.3.1 Nitrogen and Phosphorus Acquisition from Wastewater*

High nitrogen (N) and phosphorus (P) contents resulted in eutrophication and associated ecological issues in water sources. So removal and utilization of these minerals are an essential part of sustainable development. The nitrification and denitrification process activated by *Scirpus validus*, *Phragmites communis*, and *Typha latifolia* reduced the N content in the wastewater. Of these three plants, *S. validus* and *P. communis* showed better N removal, and this efficiency depended on the $O_2$ transportation from shoot to root (Deng et al. 2020). *Salicornia europaea* and *Aster tripolium* are the two halophytic plants used to remove N content from municipal wastewater (Quintã et al. 2015). The macrophytes and algae also aid in the removal of pollutants, especially the excess N and P content, and the organisms involved in the study include *Eichhornia crassipes*, *Microcystis aeruginosa*, *Scenedesmus falcatus*, *Chlorella vulgaris*, and *Chlamydomonas mirabilis* (Tripathi and Shukla 1991). *Chlorella vulgaris* is a microalga cultivated in wastewater to analyse removal kinetics of N and P. It was found that this organism has high N removal capacity but is inefficient for P removal from wastewater (Zimmo et al. 2004; Aslan and Kapdan 2006). This study indicates the utilization of a single organism for the purpose of P removal is not efficient, and thus the algal turf scrubber was introduced in the field of wastewater remediation (Craggs et al. 1996; Siville and Boeing 2020). Algal turf scrubber consist of fixed periphyton, microalgae, and bacteria, which aid in remediating eutrophic water sources (Siville and Boeing 2020). An algal turf scrubber efficiently removed P and simultaneously it is used for the production of algal biomass (Siville and Boeing 2020). Moreover, the optimization of the action of algal turf scrubber depends different factors like pH balance, types of algal attachment substrates, water flow conditions, temperature, and hydraulic loading rate (Salvi et al. 2021).

In a comparative study conducted between the microalgae consortium and *Chlorella vulgaris*, the microalgae consortium showed better N and P removal from wastewater. Moreover, this consortium had maintained biomass production by utilizing mineral ions (Lage et al. 2021). *Palmaria palmata*, red macroalgae have high N removal efficiency. This species has a different affinity towards nitrogen sources; i.e., the affinity was higher towards $NH_4^+$ than for $NO_3^-$. Simultaneous to the removal rate of N, there was an increase in mineral assimilation and protein biosynthesis in *P. palmata* (Grote 2016). This indicates that different aquatic plants and algae could be used as potent candidates for N and P removal, but on comparison between these organisms, it was pointed out that algal ponds had more efficiency than a plant (*Lemna gibba*) based pond for the removal of mineral ions (Zimmo et al. 2004).

Different crop plants play a significant role in wastewater remediation when it is used for irrigation purposes. When *Zea mays* and *Vicia sativa* were treated with wastewater, these two plants had augmented uptake of macro and micronutrients (Mohammad and Ayadi 2004). This showed that the N removal efficiency was increased due to the crop mediated uptake, whereas the P removal was achieved with different soil processes (Yang and Kim 2020). Nitrification of ammonia in the effluent by soil microorganisms also promotes the removal of N from irrigating wastewater (Deng et al. 2020).

### *8.3.2 Utilization of Organic Waste as a Source of Energy*

Organic waste materials are one of the significant components of wastewater, and these carbon-rich sources increase the multiplication of algae and the growth of aquatic plants. The increase in biomass production and subsequent biofuel production mainly depends on the organic matter in wastewater (Cui et al. 2020). Algae and cyanobacteria aid to remove the excess C content in the wastewater coupled with the transformation of this C into the valuable biomass (Cui et al. 2020). *Chlorella sorokiniana* was used to produce biofuel from food waste, and the same organism aid in the removal of excess N and P content in the water (Chi et al. 2011). High rate algal ponds (HRAPs) using wastewater with a high C:N ratio is a good strategy for biomass production (Sharma et al. 2020). Activated algae with the bacterial combination is another strategy for removing organic components from wastewater by the production of biofuels (Xu et al. 2021).

*Nelumbo nucifera* and *Hydrilla verticillata* were also used for the removal of organics from wastewater. In this study, the difference in the BOD was used to analyse the efficiency of these two plants, and *N. nucifera* had a better organics removal capacity than the other one (Kanabkaew and Puetpaiboon 2004). The aquatic plants such as *Scirpus validus* and *Phragmites communis* also had a high BOD removal efficiency (Deng et al. 2020).

### *8.3.3 Heavy Metal Uptake and Utilization*

Aquatic plants and algae have enhanced potential for the bioaccumulation of toxic metal ions to the biomass in large quantities compared to the terrestrial plants (Wani et al. 2017). Upon exposure to the metal stress, these plants produce cysteine-rich metal-binding proteins called phytochelatins (PCs), which help to scavenge and detoxify the metal ions from the cytoplasm by forming stable complexes. Török et al. (2015) conducted a study to analyse the efficiency of heavy metal removal in three aquatic plants such as *Elodea Canadensis*, *Salvinia natans*, and *Lemna minor*, and it was observed that these plants showed higher uptake of Cu, Cd, and Zn along with higher production of γ-glutamylcysteine and PCs ($PC_2$, $PC_3$, $PC_4$, $PC_6$, and $PC_7$). It was also pointed out that, the enhanced phytoremediation capacity of these plants were associated with the increased production of PCs along with their higher degree of polymerization. According to Shukla et al. (2012), the heterologous expression of phytochelatin synthase (PCS) gene from a submerged rootless aquatic macrophyte *Ceratophyllum demersum*, resulted in the enhanced production of non-protein thiols and PCs and thereby accumulation of As and Cd in transgenic tobacco plants.

According to the study conducted by Li et al. (2015b), the aquatic plants belonging to the families Ceratophyllaceae, Haloragaceae, Poaceae, Pontederiaceae, and Typhaceae were found to be comparatively with higher potential to accumulate metal ions from wastewaters. It has also been reported that a relatively higher accumulation of heavy metals such as Cd, Cu, and Zn was observed in submerged plants compared to the emerged plants (Li et al. 2015b). It may be due to the degradation of roots in the emerged plants, which prevent the entry of toxic metals to the plant body, or the development of root-like modified leaves in submerged plants, which enhances the metal uptake.

Moreover, the higher surface area-to-volume ratio of the submerged plant enables the enhanced metal uptake (Li et al. 2015b). According to Phukan et al. (2015), *Hydrilla verticillata* has a removal efficiency of 66–76% Cr and 95–99% Cd from 5 to 15 mg/L Cr and 1–3 mg/L Cd contaminated water, respectively. Likewise, *Eichhornia crassipes* and *Typha latifolia* are the potential accumulators of As, Cd, Cu, and Pb. Of which, *T. latifolia* has the highest accumulation, with bioconcentration factor (BCF) of 1312.5 for As, 106.7 for Cd, 895.8 for Cu, and 174.6 for Pb in the leaves (Sukumaran 2013).

After successful phytoremediation practices, the plant and algal biomass can be effectively utilized to produce energy-rich compounds. These compounds generated from biological sources via chemical, biochemical, or biological processes are regarded as biofuels. Of the various biofuels, the biofuels produced by microalgae and other microorganisms constitute the third generation biofuels and are the best substitute for any other biofuels (Kour et al. 2019). Therefore, aquatic plants and algae with enhanced heavy metal bioaccumulation potential can be ideally used for the reclamation and re-vegetation of the metal-polluted waters along with the efficient production of bioenergy, which is a cost effective, economically feasible, and eco-friendly technology for wastewater treatments.

## 8.4 Challenges of Phytoremediation and Phycoremediation

During the treatment of wastewater, the degradation of the organic contaminants occurs via the activity of enzymes associated with the plants and algae. However, the degradation products may cause other effects in both plants and algae (Mustafa and Hayder 2021a). In phytoremediation processes, the detoxification and accumulation is limited to shallow range of contaminants. Therefore, the complete cleaning of the wastewater is a tedious task. Likewise, some contaminants have the potential to induce phytotoxicity, and therefore proper selection of the plant species depending on the type of contaminant is necessary.

The slow remediation rates as well as the requirement of large space for the algal cultivation are the most important challenges associated with phycoremediation technologies. Though, algae are well known for the production of pharmaceutically important bioactive compounds, the extraction of these compounds is not efficient due to the low biomass production. To overcome these situations, genetically modified algal strains can be implemented in large scale. However, growing genetically modified algal strains in open system have legal issues due to the interference of their growth to other natural strains (Krishnamoorthy and Manickam 2021).

Another problem related to algal culture is the contamination of the culture by bacteria. If a symbiotic association between algae and bacteria is essential for the treatment of wastewater effluents, the bacterial contamination may not be a problem (Bansal et al. 2018). Otherwise, the contamination issues can be overcome by the application of mild doses of antibiotics or by growing the algal strains in completely sterilized photobioreactors, but both are expensive. Similarly, growing algae in photobioreactor requires a constant supply of $CO_2$, which is also expensive and needs huge efforts. The light energy absorbed by the photobioreactor which is not utilized for photosynthesis, is converted to thermal energy; resulted in the increase in temperature in the culture system, and thereby failure of the whole culture system (Wasanasathian and Peng 2007). Therefore, detailed research is required regarding the optimized operating conditions of photobioreactors especially the temperature control.

## 8.5 Conclusion and Future Perspectives

The entire biosphere is under the threat of environmental pollution, and among them, water pollution is more severe because it is a vital component of all living organisms. The ever-increasing population, human manipulations, and overuse of natural resources are continuously depleting the quality of drinking water. In this scenario, the remediation using natural techniques can be applied as a suitable method for remediation or treatment of wastewater. The easy biomass production, cost-effectiveness, lesser energy input, and prospecting of treated plants for bioenergy forms have given much importance to this biological means of wastewater treatment. Application of the transgenic approach for producing much more tolerant plants for the decontamination purpose will be an area of good research. The application of these plants with potential chelating capacity to improve the remediation potential of the biological agents is less studied. The remediation and utilization of the remediating agents for the production of nanoparticles and their application in biosensors have not been studied well. So the area of green remediation opens up several other interdisciplinary applications.

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# Chapter 9
# Application of Nanomaterials for the Remediation of Heavy Metals Ions from the Wastewater

**Lata Rani, Jyotsna Kaushal, Arun Lal Srivastav, and Gagandeep Kaur**

**Abstract** Due to the fast growth of industrialization and urbanization, the water pollution has been reached to alarming stage, which leads scarcity of safe drinking water. The heavy metals are non-biodegradable and they are bioaccumulated in living organism. This results in chronic health to animals as well as human beings. Therefore, remediation of heavy metal ions from wastewater become the urgent thirst of current world scenario. There are various remediation approaches such as ion exchange, adsorption, membrane filtration, coagulation, flocculation, floating, and electrochemical applied for the removal of heavy metals from wastewater. Among them adsorption is the optimized approach due to high efficiency and production of less harmful by-products. Earlier various materials such as cellulose, waste material, activated charcoal, minerals, etc. were applied as adsorbent. Nowadays nanotechnology emerging as efficient remediation technology for heavy metals and researcher attracted towards the application of nanomaterial as adsorbent. In this chapter discussion has been carried on application of various nanomaterials for the wastewater treatment.

**Keywords** Nanotechnology · Heavy metals · Water treatment · Adsorption

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## 9.1 Introduction

The most abundant natural resource available on earth is water of which only about a percent is accessible for personal use (Grey et al. 2013; Adeleye et al. 2016a, b). Anticipation was earlier done that more than one billion population lacks in the adequate supply of desired quality water (WHO 2015), due to the ratio of raising expenses for consumable water, increasing population, and a heap of environmental and climatic issues (Adeleye et al. 2016a, b). Majority of the confrontations posed in supply network of water is constantly polluting new water assets by an assortment of natural and inorganic contaminants (Schwarzenbach et al. 2006). Treating both wastewater and drinking water can decrease these fears (Ferroudj et al. 2013); however, the customary age old strategies used for treatment are not so effective so as to completely eliminate different kind of impurities and fulfill the standard criteria of water standard guidelines (Qu et al. 2012). In addition, the current expertise of nonpotable water medicines also have few disadvantages like high-energy requirement, inadequate toxin clearance, and ages of toxic sludge (Ferroudj et al. 2013). The natural wastewater treatment is commonly used because of several reasons like these are characteristically thorough, restricted due to the occurrence of non-biodegradable impurity, and at some point may be toxic to the microorganisms (Zelmanov and Semiat 2008). The physical operations, for example, clarification can completely eliminate the impurities by changing over phases delivering an exceptionally solid slurry (Catalkaya et al. 2003; Bali et al. 2003), which are poisonous and tricky to discard.

As stated for the above situation, there is incurring prerequisite and that is for more proficient and incredible innovations needed for the treatment of city and modern wastewaters (Burkhard et al. 2000; Parsons and Jefferson 2006; Crini and Badot 2007; Ferroudj et al. 2013). This can be accomplished using either stepping up to usage of totally new techniques or by working upon the currently used strategies through certain modifications. Among the advent of various advancements, nanotechnology has come up as an unimaginable potential for the remedies of wastewater and many other ecological issues (Zare et al. 2013; Sadegh et al. 2014; Gupta et al. 2015). Nanotechnology is a broad region of nanoscience as a whole that work wonders on a very small scale of nanometer. Nano-substances are tiniest of all the structures, created up to date till now, having dimensions of a nanometer (Chaturvedi et al. 2012a, b). To say more accurately the nanomaterials are the particles that have a configuration having dimensions even smaller than 100 nm (Amin et al. 2014). Nanostructures are often used to build various substances from it like wires, membranes, particles, dots, tubes, quantum dots, and colloids, among other things (Lubick and Betts 2008).

Treatment of wastewater when applied, a proficient group of practical and organic nano-substances are established having interesting arena for possible sterilization of industrial waste material, and waters including surface, ground, and drinking water (Brumfiel 2003; Theron et al. 2004; Gupta et al. 2015). Nanotechnology is one of the most exceptional techniques for wastewater treatment by most of the science groups. It is well classified into three fundamental categories, i.e. nano-adsorbents, nano-catalysts, and nano-membranes. In nano-adsorption innovative technique, various viable works have been listed with the expectations to examine the elimination of contamination (Sayan et al. 2013).

Nano-adsorbents can be provided by using particles of all those enrich fundamental elements that are synthetically energetic and have a high adsorption capability on the surface of nano-substance materials (Kyzas and Matis 2015). There sources to be utilized for improvement of small scale absorbency incorporated activated form of carbon, mud materials, silica gel, oxides of metal, and customized chemical amalgams in the form of hybrids (El Saliby et al. 2008).

Nano-catalysts are a subsequent form of nanomaterials. Researchers have given nanomaterials including oxides of metal and semiconductor materials a lot of thought when it comes to developing wastewater treatment methods. For the degradation of wastewater contamination, several types of nano-catalysts are used, such as electron based catalysts (Dutta et al. 2014a, b), "fenton-based catalysts" (Kurian and Nair 2015) for recovering chemically oxidized natural contaminants (Ma et al. 2015a, b) and catalysts holding antibacterial activity (Chaturvedi et al. 2012a, b).

Nano-membranes belongs next category of nanomaterials that have been exploited in wastewater treatment. Pressure-controlled treated water has been shown to be suitable for ensuring the standards of desirable water in that unique technology (Rao 2014). Among several known kinds of membrane filters (Lau and Ismail 2009; Ouyang et al. 2013; Blanco et al. 2012), nano-filters (NF) are most extensively used for processes involved in treating wastewater in businesses for the reason of its smallest pore size dimensions, low cost, great competence, and ease of usability (Petrinic et al. 2007; Hilal et al. 2004; Babursah et al. 2006; Rashidi et al. 2015). Nano-membranes can be created from nanomaterials, for example, metal nanoparticles, non-metal nanoparticles, and nanocarbon tubes are only a few examples (El Saliby et al. 2008). Several studies are being conducted to assess the efficacy of several recently developed nanomaterials. In this chapter, there will be discussion on four different types of nanomaterials and how they can be used in treating wastewater. Nano-adsorbents, nano-impetuses, nanofilms, and the blend of the all the above mentioned nano innovations with natural techniques are among them.

Because of broad industrialization and urbanization over the past hundreds of years, a lot of substantial metal particles keep on being released into the climate by human activities for example, electroplating, mining, synthetic manufacturing, and the utilization of pesticides and composts (Ok et al. 2010; Li et al. 2018; Yu et al. 2020). Heavy metal poisoning in soil and water has turned into a disastrous issue for some of the nation's worldwide (Sall et al. 2020; Liu et al. 2020). Due to the non-biodegradable, and poisonous nature of heavy metals, like chromium, mercury, cadmium, lead, and copper, the biological atmosphere and human well-being are genuinely compromised (Vilardi et al. 2018; Yu et al. 2019; Hou et al. 2019). For instance, the microbial growth in soils tainted with metals such as Cd, Pb, and Cr is truly restrained (Nagajyoti et al. 2010). Additionally, even low presence of heavy metals in the nature might cause genuine ecological and medical conditions

(Alidokht et al. 2011; Yu et al. 2014). Consequently, to secure the biological climate and public wellbeing, elimination of these substantial metal particles is a necessity.

Contamination of any kind is basically the presence of any undesirable chemical entities that obstruct biological processes or have negative consequences for living beings and the environment (Mehndiratta et al. 2013; Nimibofa et al. 2018; Yu et al. 2019). Pollution has increased at such an alarming rate because of industrialization and the massive urbanization (Zhang et al. 2017; Madhav et al. 2021). Improvising the features of water, soil, and air is a huge problem in today's world so is the identification, treatment and prevention of this critical problem. Material science played a significant role in achievement of the cleaner environment, and this technology has advanced at an exponential rate in recent years (Mauter and Elimelech 2008).

Due to industrialization, pure and clean water has become rare in modern era, and the globe all over is experiencing a deficiency of desired and hygienic water, particularly in poor countries (WHO 2017). Water is the main carrier of most of the non-biodegradable chemicals such as organic dyes, bacteria, different viruses, and last but not the least heavy metal ions, all these pose a significant risk to human health. Different cancers, kidney damage, liver disorders, loss of blood, miscarriages, and nephritis are all possible side effects of heavy metal ions (Sardans et al. 2011; Baby Shaikh et al. 2018; Yang et al. 2018; Bali and Tlili 2019). Various processes like metal mining, lead battery manufacturing, paper, glass, and polishing sectors all liberates lead ions into the atmosphere. Also, water liberated from electroplating and metallurgy techniques involved in designing of batteries and inverters act as main source of cadmium in environment, the sources of heavy metals in water as shown in Fig. 9.1 (Wang et al. 2012). When nickel ions come into touch with jewelry, zips, coins, and supplementary metals, they can cause skin disorders. Chromium ions (VI) is responsible for disturbances of various organs including kidneys, liver and lungs or gastric tract, nasal mucosal ulcers, etc. (Moreno-Castilla et al. 2004).

Due to the serious side effects, exclusion of all these poisonous ions from available water becomes so critical for preservation of human health. Ion exchange, precipitation filtration, coagulation, reverse osmosis, biosorption, and extraction are some of the customary ways for removal of lethal metal ions (Fu and Wang 2011; Huang et al. 2018). Adsorption is one of the finest approaches for elimination of trace quantities of heavy metal ions since it is lucrative, extremely efficient, and ease of use (Czikkely et al. 2018). For water treatment, several materials have been utilized, including organic adsorbents particularly humic acid, that is widely exploited for disinfecting water and heavy metal ion elimination (Hankins et al. 2006; Parvin and Hoque 2016; Huang et al. 2018). Tang et al. (2014) provided a thorough evaluation of humic acid itself and its nano-derivative in water handling. Almost all sciences whether it be environmental or health related, and even electronic industry, water treatment plants may be large or small scale, are just the minority of the fields where nanotechnology platforms are playing a great role (Zeng et al. 2016; Zeng et al. 2018; Liu et al. 2018). Because of their enormous

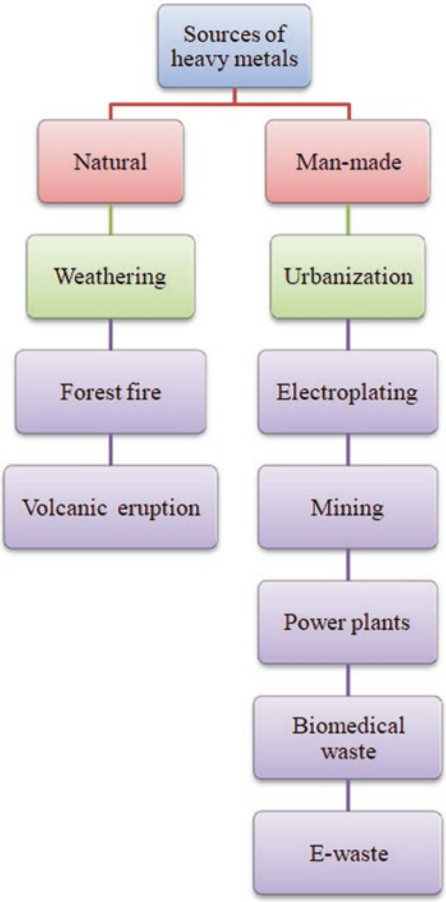

**Fig. 9.1** The sources of heavy metals in the water

surface area, chemical modification capacity, and ease of regeneration, nanomaterials are providing a unique foundation for the refinement of unhygienic water. Nanomaterials are increasingly being used to remove several types of pollutants from water, including organic and inorganic waste (Bradder et al. 2011; Al-Senani and Al-Fawzan 2018; Bozbaş and Boz 2016; Brunet et al. 2009).

Owing to their extraordinary characteristics, carbon nanomaterials such as fullerenes, graphene, and their oxides, and nanotubes, have been exploited widely in storing energy, constructions of nanosensors, water sanitizing techniques, drug delivery systems, disease diagnosis, and various other applied fields. Attempts has been accomplished to discuss the most recent advances in the use of organic nanomaterials aiding in the purification of lead and other metal ion-contaminated water in this article.

## 9.2 Toxicity of Heavy Metals

Heavy metals on an average are known by their molecular formula and weight, but the term can also be applied to metals that can act as poison to living organisms (Appenroth 2010). Several heavy metals prove to be harmful in variety of forms and to different extents to human health and other living organisms (Table 9.1). Heavy metals are frequently assumed to be toxic; however, some lighter metals, such as beryllium and lithium, can also be harmful. It is not like that all the heavy metals are toxic for one's health but some are vital, such as iron and Cr(III) while Hg, Pb, Cr, Cd, Mn, As, and radioactive metals are the majority of well-known risky metals. Radioactive metals are shown to be associated with both radiological and chemical toxicity as well. Heavy metal toxicity laid foundation for a large number of health risks. Moreover they can also enact as a part of our body, interfering metabolic and other biological processes. Very few metals, like aluminum, are hurriedly removed with excretion system, whereas others get accumulated in the eco system causing health concerns. There are several factors affecting toxicology caused by metals like dosage, administration route, and time of stay in body (e.g., acute or chronic). The following section details the toxicity of several heavy metals.

## 9.3 Nanomaterials as Adsorbents

Since the debut of the scanning tunnel microscope (STM) in 1980, nanotechnology has been investigated. Nanoparticles are particles with a dimension ranging from 1 to 100 nm that have specialqualities such as a high specific surface area, high magnetic selectivity, and improved chemical aand physical surface interfaces, all of which support their use in the removal of contaminants (Mehndiratta et al. 2013). Metallic nanoparticles, magnetic nanoparticles, carbon nanotubes (CNTs), and nanofillers have all been manufactured in the past few years using diverse methods

**Table 9.1** Adverse effects of heavy metals contamination in water on the health of human beings (Fahimirad and Hatami 2017; Yahaya and Don 2014)

| S. No. | Heavy metals | Chronic effects |
|---|---|---|
| 1. | As | Carcinogenic, skin rashes, bronchitis |
| 2. | Cd | Kidney disorder, respiratory syndrome |
| 3. | Cr | Respiratory disorder, CNS syndrome, cardiovascular syndrome. |
| 4. | Mn | Harm to CNS |
| 5. | Hg | Paralysis, Carcinogenic, mutagenic, damage of CNS, damage of liver |
| 6. | Pb | Reproductive disorder, Renal disorder, decrease in IQ level of infant, CNS disorder, liver failure |
| 7. | Cu | Renal disorder, stomach infection, failure of liver |
| 8. | Zn | Damage of neural, nausea, dermatitis |

(Huang et al. 2018). Because of their great potential for adsorbing pollutants, nano-adsorbents are utilized in treating wastewater. Waste water treatment utilizing nanoparticles works on the criteria of thermodynamic efficacy and making the maximum use of chemical strength to achieve equilibrium between the different phases and also the strength of the chemical reaction upon which elimination of waste material is based (Czikkely et al. 2018).

## 9.4 Metal Oxide Nanoparticles

The band gap of the alkoxides is the major distinction between micro/macro and nano scales; as particle size decreases, so does the band gap, which significantly effect conductance and reactivity of chemicals (Fernández-Garcia and Rodgriguez 2007). Moreover, it is due to the structuring of ternary ligands, metallic oxides of the nanomaterials displayed greater adsorption than conventionally used oxides (Stietiya and Wang 2014). The removal effectiveness of heavy metals on nonabsorbent of Zn, Cu, and Fe oxides were strongly depended on the pH of the untreated water solution. Because of ionic bonding, types of precipitation, and the creation of metal complexed compounds with electrostatic or covalent interactions, the elimination of heavy metals from corresponding solution increases as pH value increases. The total process depends upon the chemical relationship between metal and its solution and also on the nature of functional groups attached to it. The attraction forces between the negative side (adsorbent) and the positive side (solvent) cause deprotonation at the nonabsorbent surface, increment of electronegative charge, and adsorption capacity as consequential effect. Lowering pH, on the other hand, smoothen the process of competitive adsorption that occurs between metal and solution ions (Mahdavi et al. 2015). The optimum adsorption capability of Ferric oxide for lead(II) ions was 36 mg/g, according to numerous studies, with equilibrium attained in a time even lesser than 30 min. This process is known to be endothermic, and the number of lead ions that got absorbed has also been shown to increase as the temperature value rises (Nassar 2010). According to investigations, anatase based nanomaterials biologically synthesized by the solgel method had the supreme uptake capacity for the exclusion of different ions including that of arsenic, copper, lead, with values, respectively, of 17 mg/g, 24.1 mg/g, and 31.3 mg/g. The adsorption capacity of lead and copper ions was governed by pH, whereas in the case of arsenic ions, pH had no effect (Kocabaş-Ataklı and Yürüm 2013). In 2013, a nano-adsorbent with an average size of 3.7 nm, a specific surface area of 438.2 $m^2$/g, and a precise magnetization of 32.9 emu/g was successfully fabricated by doping Ferrites with 10% $Mg^{2+}$ using thermal treatment that make them ideal for wastewater rectification. At neutral pH, the adsorption capacity of As(III) ions was 127.41 and 83.25 mg/g for As(V) ions (Tang et al. 2013). In 2013, another nano particle was discovered as an Arsenic and Arsenious ions adsorbent for wastewater treatment. Manganese feroxyhyte (-Fe0.76 Mn0.24OOH) nanoparticles were produced using the coprecipitation technique. For coprecipitation of $FeSO_4$ and $KMnO_4$, a powerful oxidizing agent was applied, resulting in an uniformly dispersed crystal structure. At a neutral pH, the nanoadsorbent was examined on potable water and found to have a prospective deduction capacity of 6.7 g/mg for As(III) and 1.7 g/mg for As(V) (Tresintsi et al. 2013). In 2014, Fe-La nanoparticles were produced and evaluated as an adsorbent for the separation of As(III) from wastewater. The merged compound carries the same crystal structure as of Lanthanum oxide and displays maximum As(III) adsorption ability of 58.24 mg/g in a neutral pH solution. A maximum adsorptive capacity of Zn(II) ions was attained using an alumina ($Al_2O_3$) nanoadsorbent for the separation of Zn(II) ions from wastewater (Covaliu et al. 2019).

## 9.5 Magnetic Based Nanoparticles (MNPs)

Nanoparticles based on superior paramagnetic effect offer various characteristics like being not as much of poisonous, biodegradable, chemically stable, having a low diffusion resistance, and the ability of surface to modify facilitates heavy metals removal from wastewater utilizing organic molecules, inorganic ions, or certain functionalities. MNPs will be more stable as a result of the surface area changes since oxidation will be inhibited. Physical as well as chemical and chemical including those of bonding, complex formation, electrostatic or modified ligand binding interactions are involved in the adsorption of heavy metal in ionic form from wastewater (Patwardhan et al. 2012). Mercury ion elimination from wastewater was achieved using mercapto-functionalized nano-ferricoxide magnetic polymers (SH-$Fe_3O_4$-NMPs). At a temperature of 35 °C and a pH of 3.0, MNPs demonstrated great efficacy. The adsorption effectiveness grows as the pH value rises. The constants were calculated and tabulated using the Freundlich isotherm equation (Pan et al. 2012). The thermal breakdown of FeOOH was investigated for the manufacture of Carboxymethyl bound cyclodextrin molecules specially monodispersed magnetic nanocrystals and 10 nm particles for the removal of arsenic in both oxidation states, naphthalene and naphthol from wastewater. Nanocrystals were effective for wastewater treatment after a sole period of magnetized phase separation (Chalasani and Vasudevan 2012). The hydrothermal process was utilized to make superparamagnetic ferric oxide nano hybrid compounds that were coated with ascorbic acid, and used to remove arsine from wastewater. The nanocomposites that were created have diameters of less than 10 nm. Arsenic ion(III) clearance had the maximum adsorption capacity of 16.5 mg/g, while Arsenic(V) elimination had the highest adsorption capacity of 46.1 mg/g (Feng et al. 2012). Hg(II) ion removal was tested on both unaltered and altered ferric oxide magnetic nanoparticles. The initial mercury ion(II) concentration was found to be 50 ng/mL, and the yield for unmodified nanoparticles was almost 43.4% and for changed nanomaterials was around 98.12% (Parham et al. 2012). Manganese iron oxide magnetic nanoparticles were covered with Mn-Co amorphous oxide shells, yielding a hybrid with a considerable negative charge across the pH range. Pb(II) removal had the highest adsorption capacity of 481.21 mg/g, followed by Copper(II) removal at 386.4 mg/g, and Cd(II) removal at 345.3 mg/g (Ma et al. 2013) The manufacture of iron oxide loaded nanosorbent for the elimination of Eu(III) ions from wastewater was accomplished using the coprecipitation approach. The magnetic nanoparticles produced have an active surface area of 85.11 $m^2$/g, a mean particle size of 63 nm, and heat resistance of above 600 °C. At a pH of 2.5, 5 mg of adsorbant were employed to achieve an equilibrium power of 157.14 mg/g in time lesser than 12 h. Ferrous oxide nanocomposites of cellulose were synthesized using a chemical coprecipitation process and utilized to treat arsenic-polluted wastewater (Yu et al. 2013). Due to their sensitive magnetic characteristics, compounds had a surface area of 113 $m^2$/g and were simply separable, with optimum removal capacities of 23.1 mg/g and 32 mg/g for As(III) and As(V), respectively (Moussa et al. 2013). The surface of iron oxide nanoparticles was coated with thiosalicylhydrazide, resulting in magnetized nanosubstances for heavy metal ion exclusion from aqueous media. Pb(II) had a value of 188.2 mg/g, Cd(II) had a value of 108.4 mg/g, Cu(II) had a value of 77 mg/g, Zn(II) had a value of 51.5 mg/g, and Co had a value of 28.2 mg/g (II). The added benefit of modified nanoparticles is that they are recyclable and environmentally beneficial (Zargoosh et al. 2013).

## 9.6 Carbon Nanotubes (CNTs)

Carbon filled nanotubes have a distinctive constitution and a number of properties, including mechanical strength, specific surface design morphologies, conductance, and optical activity. Their low mass bulk, greater porosity of surface, higher surface area, robust impurity acquaintances, and hollowed arrangement further make them ideal alternatives for nano absorbents (Dresselhaus and Avouris 2001). Carbon nanotubes have four ideal separate sites for adsorption phenomenon due to their unique structure: interstitial channels, exterior surface grooves, and interior sites, along with external sites reaching balance sooner than internal sites. Chemical interactions between the surface of material used in nanotubes and metal ions are the primary cause of their adsorption capabilities. Depending on the production and purification procedure, carbon nanotubes can have diverse functionalities like that of carboxylic, carbonyl or hydroxyl groups. By oxidation of carbon nanotubes with catalysts like Ni, Pd, or Pt, they can be seeded with desired functional groups. Hexane, cyclohexane, and benzene are hydrophobic groups that are favored above hydrophilic groups like alcohol. The preference can be reversed by altering the hydrophilicity of CNT surfaces. When the protons are released, pH of the solution drops (Lu et al. 2006; Gotovac et al. 2007). Maghemite nanotubes were created using the microwave irradiation process. They had a specific surface area of 321.6 $m^2$/g and a magnetic saturation of 68.7 emu/g. The removal of Pb(II), Cu(II), and Zn(II) from these nanotubes was examined, yielding the following adsorption values for different ions like lead (71.5 mg/g), Zinc (83.1 mg/g), and Copper (111 mg/g) (Roy and Bhattacharya 2012). A magnet fused nano hybrid compound was created as a multiple walled carbon based nanotube for the adsorbing of mercury and lead from wastewater. The adsorption capacity of Hg(II) is 65.52 mg/g, while that of Pb(II) is 65.40 mg/g (Zhang et al. 2012). A newer application of magnetic multiple walled nanotubes is the confiscation of Nickel(II) from effluent. Purified multi-walled carbon based nanotubes were subjected to a high-temperature treatment with strong sulfuric acid. The synthesized carbon nanotube has been put to the test in Cu(II)-polluted water. Cu(II) adsorption capacity rate was found to be 58.9% after sulfonation (Ge et al. 2014). Chemical vapors of cyclohexanol and ferrocene get deposited at 750 °C was used to make CNTs, which were then treated with nitric acid and chitosan in the presence of nitrogen. At the starting concentration of 800 mg/L, the adsorption capacity of Cu(II) ions got an increment from 24.33 deprived of functional groups attachment to 58.33 mg/g after derivatization (Tofighy and Mohammadi 2016). Carbon nanotubes having magnetic character were fabricated by means of a damp chemical approach intended for the deletion of Chromium(VI) ions from sewerage water. Concluding from the results stated above, it was found that adsorption competence is directly proportional to contact duration and concentration of metal ion but inversely related to adsorbent dose. Endothermic and continuous processes are involved in above said reactions (Huang et al. 2015).

## 9.7 Chitosan Formulated Nanomaterials

Chitosan is the side product of the processing of shellfish waste. It is a biopolymer made up of natural polysaccharides that is a superb adsorbent since it is plentiful, chemically stable, cheap, nontoxic, hydrophilic, biodegradable, renewable, biocompatible, and has a high reactivity for a variety of contaminants. It has good adsorption capabilities for hazardous metal ions due to occurrence of an amine group ($-NH_2$) in the polymeric matrix and a partially positive charge. Strongly magnetic chitosan nanoparticles have an excellent adsorption efficiency. Because the exchanges occurring across chitosan and heavy metal ions are in reversible mode, that is why magnetized chitosan nanoparticles can be retrieved using a magnetization following wastewater depollution (Liu et al. 2009; Jassal et al. 2015). Synthesized dual oxide coated chitosan having an adsorbing power of 16.94 mg/g were used to remove As(III) from wastewater. Ca(II) and Mg(II) were discovered in wastewater, affecting the As(III) removal process. The adsorption procedure proved ineffective in the pH range of 3–9. The content of Arsenic(III) was lowered to 7.44 g/L from 983.7 (Dhoble et al. 2011). The Box–Behnken approach was utilized to produce "chitosan-coated magnetic NPs" that were exploited to remove mercury(II) ions from unhygienic water. A percentage yield of 99.1 was attained using 0.67 g of adsorbing material, observed at pH of 5 taking initial concentration of mercury ions at 6.22 mg/L. The exterior surface of chitosan-coated magnetite nanoparticles has a high density of active sites (Rahbar et al. 2014). The adsorption of Copper(II), Cadmium(II), Zinc(II), and lead(II) ions on magnetic coated nanoparticles was also investigated, with a considerable decrease in ionic concentration in wastewater (Jassal et al. 2015). The process of deacetylation of chitin has been investigated for the production of chitosan formulated nanoparticles for the deletion of Manganese(II), Zinc(II), Ferrous(II), and Copper(II) ions. At neutral pH, an early contamination with concentration around 20 mg/L, and a mixing interval of approximately 30 min, 2 g/L of adsorbent was added to the solution. Fe(II) had a removal efficiency of 99.94%, Mn(II) had an efficiency of 80.85%, Zn(II) had a removal efficiency of 90.49%, and Cu(II) had a removal efficiency of 95.93% (Kaushal and Singh 2017). For excluding Copper(II) and Lead(II) ions present in wastewater, various composite nanofiber comprising chitosan and $TiO_2$ being manufactured using a coating and entrapment technique. The entrapment approach had optimum adsorption efficacy of 526 mg/g for Cuprous(II) ions and 475 mg/g for lead(II) ions. Nanofiberous substances from the entrapment process can be reprocessed with the same performance after five desorption rounds. In the first phase, only 60% of the coating approach's adsorption yield was achieved (Razzaz et al. 2016).

## 9.8 Silica Based Nanomaterials

Silica would be a substance that is utilized as a shell for nanoparticles in wastewater depollution studies. The coating method of the silica formed nanomaterials, activates their surface, carrying variety of functionalities. Silica also preserves nanoparticles in solutions with low pH. When the filler content is minimal, polymer layered silicate nanocomposites have better characteristics. At neutral pH, the acid character of nanoparticles based on silica intensifies with the particle size resulting in a 5–20% dissociation of silica groups.

The anionic shell of silica fascinates cations as a consequence of ion pairing. Silica formed nanoparticles, silicon or graphite oxides, and nano sized graphites as adsorbents were used to remove lead, zinc, chromium, and various other heavy metals present in wastewater. Ni(II) > Zn(II) > Pb(II) > Cd(II) > Cr(II) > Ni(II) > Zn(II ) > Pb(II) > Cd(II) > Cr(II) > Cr(II) > Cr(II) > Cr(II) > Cr(II) > Cr(II) > Cr(VI). Graphite oxide was another adsorbent that performed well in the nickel removal process. Write between the three, the silica or graphite oxide with a 2:3 ratio was the most efficient adsorbent for wastewater depollution (Sheet et al. 2014). Microparticles of activated carbon having an average particle dimension of 25 nm, nanoparticles founded on silicon base and a silica activated carbon nano compounds with a same ratio with a usual particle magnitude of 12 nm were used to study the adsorbing capacity of chromium, lead or nickel, and so on from wastewater. When compared both the forms of nanomaterials, the active form of carbon and silica nanoparticles, it was found that silica fused particles displayed higher adsorption with a difference of 2:3 for corresponding nickel ions in aqueous form (Karnib et al. 2014). Silica fumes formerly treated at high temperature with concentrated nitric acid are utilized to generate amino functionality altered silica nanoparticles. These nanoparticles were primarily applied for eliminating mercury, zinc, lead, cadmium, and copper ions present in sewer water, with copper, mercury, and lead ions adsorbing with exceptional effectiveness (Kong et al. 2014). By entrenching silica cum magnetized nanoparticles in cetyltrimethylammonium ammonium bromide and using 3-aminopropyltriethoxysilane as a silane coupling agent, mesoporous silica nanoparticles were generated. Cr(VI) ions have been removed from wastewater using these nanoparticles. The researchers came to the conclusion that the output differentiates depending on the pH level. Semiporous silica based small sized particles had a high elimination rate for heavy metallic impurities, were calmly regenerated, and could be separated using an external magnetic power before being reused (Araghi et al. 2015). Mesoporous nanoparticles of silica namely MCM-41 were produced and imbedded using poly-amide as an auxiliary matrix for Mercury ions (II) adsorption from wastewater. High specific surface area and greater pore size were identified as characteristics of these nanoparticles.

## 9.9 Graphene Based Nano-Adsorbents

Graphene is an allotropic form of carbon possessing unique properties that are required in variety of environmental processes. Basically, allotrope graphene oxide (GO) is a two-dimensional carbon nanomaterial that is made by chemically oxidizing a graphite sheet. The Hummers method is the most widely utilized method for GO synthesis (Lingamdinne et al. 2016b). The water dissolving moieties in GO were tempted, which necessitated a unique oxidizing procedure (Gopalakrishnan et al. 2015). Heavy metal adsorption is enhanced by the occurrence of specialized functional groups like hydroxyl and carboxyl (Liu et al. 2009; Lingamdinne et al. 2016a, b). Due to its high surface area, mechanical strength, light weight, flexibility, and chemical stability 4900 M, GO is gaining increased attention as a strong adsorbing material for the deletion of these heavy metals (Gopalakrishnan et al. 2015; Taherian et al. 2013). Furthermore, the incidence of a functional group present on the GO surface influences the adsorbing progression (Zare-Dorabei et al. 2016). When compared to other nanomaterials like CNTs, GO has two distinct characteristics. For starters, single layers GO contains basal surfaces in two-dimensional planes for maximal heavy metal adsorption. Second, it has a simple synthesis procedure that involves chemical exfoliation of graphite without the use of a metallic catalyst or sophisticated equipment (Santhosh et al. 2016). Furthermore, because GO already has a hydrophilic functional group, it did not entail any additional treatment with acids or alkalis for improving its adsorption strength (Zhao et al. 2011). Nanomaterials based on grapheme were employed by a number of studies to adsorb several heavy metal poisons from contaminated water (Azamat et al. 2015; Dong et al. 2015; Vu et al. 2016; Zare-Dorabei et al. 2016). Ding et al. (2014) looked at removing impurities existing in wastewater using “GO-enabled technique” that utilized sand as a strainer in a column reactor. Also, Lee and Yang (2012) combined both graphene oxide and titanium dioxide to create a hybrid complex for the removal of various heavy substance ions from water. Lead, Cadmium, and Zinc ionic adsorption capacities of hybrid composites are 65.5 mg/g, 73 mg/g, and 89.1 mg/g, respectively. The removal of heavy metals from wastewater is particularly efficient with graphene and its various composites. Nonetheless, successfully reducing GO to pristine graphene material remains a major issue, as this reduction may compromise the material's mechanical and electrical properties (Santhosh et al. 2016).

## 9.10 Factors Affecting Adsorption Processes

Temperature, proton count, incubation duration, and adsorbent dosage are some of the factors that affect the adsorption process of heavy metal present in wastewater. pH affects the heavy metal impurities adsorption from wastewater, according to Srivastava et al. (2015). At pH 5.5, Zinc ions (II) adsorption on magnetic surface of nano-adsorbent reaches its maximum; however, as pH rises, adsorption declines.

Lingamdinne et al. (2016a) reported the maximum adsorption capacity (approximately 94% and 99%) of different ionic forms at pH of 6.0 and 4.0 for lead and chromium, respectively. For further concern, if contact duration rises, it causes an elevation in the adsorption rate of heavy metals in hydrophilic solvents as it offers a small increment of time for the process. It is observed that initial adsorption values for heavy metals is higher due to reason that they possess a higher bulk of metals in them, which so far reduces, as time upsurges due to obstruction of dynamic positions (Shirsath and Shirivastava 2015). Lingamdinne et al. (2016a) established that minimum 120 min are required for throughout adsorption for lead and Chromium ion from wastewater.

At pH 6.0 and 4.0, Lingamdinne et al. (2016a) established maximum adsorption strength of 93% and 99.6% for lead(II) and Chromium ion, respectively. Furthermore, increasing contact time improves heavy metal adsorption from aqueous solutions by giving the adsorption process additional time (Shirsath and Shirivastava 2015). Maximum adsorption of Pb(II) and Cr(III) from wastewater, according to Lingamdinne et al. (2016a), takes place in 120 min. BET surface area, surface charge, hydrophobicity, and the insertion of novel functional groups are all properties of nano-adsorbents that influence heavy metal adsorption. The adsorption capacity of nano-adsorbents is increased using these modification approaches (Tarigh and Shemirani 2013; Wang et al. 2015). Various researchers have reported on the efficacy of various nano-adsorbents for heavy metal removal, as mentioned in Table 9.1.

## 9.11 Nano-Catalysts

Researchers are paying close attention to nano-catalysts, particularly those made of inorganic materials such as semiconductors and metal oxides, in wastewater treatment applications. Electrocatalysts (Dutta et al. 2014a, b), fenton-based catalysts (Kurian and Nair 2015), and also photocatalysts (Dutta et al. 2014a, b) are used in non-potable water treatment to enhance oxidizing process of green contaminants (Ma et al. 2015a, b) and antimicrobial profile (Chaturvedi et al. 2012a, b).

## 9.12 Nano-Materials as Photocatalysts

Interactions of metal based nanoparticles with light energy forms the basis for nanoparticle photocatalytic reactions, which are of tremendous attention because to their wider and stronger photocatalytic activity for a variety of contaminants (Akhavan 2009). These photocatalysts are typically constituted of semiconductor metals that can disintegrate a variety of environmental contaminants present in wastewater, such as dyes, detergents, herbicides, and volatile chemical compounds (Lin et al. 2014). In addition, semiconductor nano-catalysts are particularly effective for the degradation of halogenated and non-halogenated organic compounds, and heavy metals in specific situations (Adeleye et al. 2016a, b). Semiconductor nanomaterials are exceedingly effective even at low concentrations and require just modest operating conditions. The photoexcitation of electrons in the catalyst is the basic operating mechanism of photocatalysis. In the conduction band, light irradiation (Ultraviolet rays in the case of Titanium dioxide) generates hollows ($h^+$) and outgoing electrons ($e^-$). Water molecules ($H_2O$) capture the holes ($h^+$) in an aqueous environment, generating hydroxyl species (OH) (Anjum et al. 2016). These moieties are a potent and indiscriminate oxidizing mediators. The hydroxyl radicals oxidize organic contaminants into aqueous and gaseous breakdown products during the reaction (Akhavan 2009).

## 9.13 Nano-Membranes

Membrane filtration technology produced with nanomaterials is the most effective solutions among current sophisticated wastewater handling techniques available (Ho et al. 2012; Zhang et al. 2013). Nanotechnology principles permitted introduction of new functionalities namely catalytic resistance, high permeation, and foul resistance, in water treatment membranes that goes besides current state of art performance (Pendergast and Hoek 2011a, b). The advantages of this technique in language of quality water after treatment, quality sanitization, and plant area requirements are the key reasons for its use (Jang et al. 2015). In addition, when compared to all available treatment procedures, it is extremely lucrative, efficient, and modest to implement (Zhou et al. 2014; Zhang et al. 2015; Guo et al. 2016). Nanofilmpartition technique is utilized excellently to eradicate all types of pollutants including heavy metals from wastewater (Jie et al. 2015). Nano-materials in new membranes play a title character in the chemical deprivation of natural impurities elimination, in addition to particle separation from wastewater (Volodymyr 2009; Yang et al. 2015). Single dimensional nanomaterials including nanofibers, ribbons and tubes comprising of both biological and non-biological materials make up the compositions of these membranes (Liu et al. 2014). A membrane constructed using carbon consisting nanofibers (CNFs) displayed outstanding selective filtration or removal efficiency under high pressure for selective filtration and nanoparticle removal (Liang et al. 2010). Furthermore, building beta-cyclodextrins for carbon based nano-membranes by a simple purification method has the ability to remove phenolphthalein and fuchsin acid with surprising efficiency (Chen et al. 2012). Zeolite-based nano-membranes can be used for aqueous osmotic separation. Sodalite, MFI-type, and Linde Type A are popular zeolite materials used in membranes. Zeolite ZSM-5 (MFI) is the most often used zeolite in nano-membranes, with a chemically composed of $Na_nAl_nSi_{96-n}O_{192}.16H_2O$ and $n \sim 3$ per unit (Pendergast and Hoek 2011a, b). Furthermore, by interconnecting nanoparticles and negatively charged substances on macroscopic disk-like titanate-nanoribbon membranes, the capturing capability of nanoparticles and other small molecules can be favorably improved.

## 9.14 Conclusion

Owing to the increase of industrialization and urbanization, the quality of water is deteriorating day by day. The provision of safe drinking water has become humanity's greatest challenge around the planet. Because of the presence of organic and inorganic impurities, the water has become tainted. The degree of pollution caused by inorganic contaminants has reached an all-time high. Metallic and nonmetallic inorganic contaminants are more dangerous because of their long-term effects on the health of both flora and fauna. As a result, an optimized remediation technique for the removal of heavy metal ions from wastewater is required. For the removal of heavy metal ions, a variety of methods are used, including flotation, membrane filtration, electrodialysis, and adsorption. However, these procedures have a number of drawbacks, including low efficiency, high cost, and secondary environmental contamination. Adsorption is one of the best ways for removing heavy metals from wastewater since it is cost-effective, easy to operate, and produces less toxic byproducts. Nanomaterials have been demonstrated to be effective adsorbents for removing heavy metal ions from wastewater. The applicability of the proposed nanomaterials for the elimination of heavy metals from wastewater was discussed by the authors in this chapter.

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# Chapter 10
# Remediation of Heavy Metals form Wastewater by Nanomaterials

**Ankita Ojha and Dhanesh Tiwary**

**Abstract** Nanomaterials have been well exploited and used for their application in environmental remediation. The role of nanomaterials swings from application in the detection of pollutants, their remediation to find a suitable substitute for the contaminants. The nanomaterials have been used for the treatment of wastewater, and there are many researchers who have defined their wide range of applications such as filters, membranes, pollutant degradation and adsorption. A variety of pollutants include physical (sediments, particulate matters), chemical (organic and inorganic), biological (microbes and pathogens) and radiological. Inorganic pollutants of wastewater primarily include heavy metal ions and anions, which are harmful to humans and may cause deadly diseases. Nanomaterials have been used extensively for the remediation of metal ions in wastewater. Silica and zeolites, which have been drawn to nanostructures, are excellent when it comes to effectiveness in the treatment of metal ions removal. Their adsorbents, as well as chelating behaviour through surface modifications, are well studied. The chapter covers various aspects of the application of nanomaterials in the field of metal ion removal, and some of these nanomaterials have been discussed here. The limitations of these nanomaterials and their plausible solutions have also been analysed in detail here.

**Keywords** Nanotechnology · Heavy metals · Water treatment · Adsorption

## 10.1 Introduction

Water is one of the indispensable needs for the survival of the human race, and imagining a world without water is worse than a nightmare. Therefore, there is an increasing need for the proper supply of drinking water as well as water for other uses. The problem of environmental pollution has become a big threat for the modern world. Rapid industrialization and urbanization have been credited to the

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destruction and damage of the environment to a greater extent. Water pollution has become a very big challenge for the existence of human beings as well as many living species in the modern world (Ahamad et al. 2020; Zamora-Ledezma et al. 2021). With the ever-increasing population, the pressure on the availability of drinking water and portable water is rising day by day. One of the biggest problems that are connected with water contamination is heavy metal ions. Heavy metals are the metals whose specific density is greater than 5 g/cm$^3$. While some of them are part of essential micronutrients for the human beings and plant world, an increasing concentration can reverse their positive effects on ecosystem (Parvin et al. 2019). Heavy metal pollution of water is one of the grave concerns of the modern world. In the metropolitans especially, this issue has become major issue of pollution because of the industrial set up around. The concentration of heavy metals in wastewater with the rising industries, especially electroplating, paints, batteries, mining and metallurgy, leather and tanning, petrochemicals, pharmaceuticals, etc. Most of the industries use heavy metals based salts for processing and synthesis purposes. Cd, Cr, Cu, Ni, Hg, Pb and Zn are heavy metals frequently used in industrial applications (International Organisation for Standardisation (ISO) et al. 2001). Both natural and anthropogenic activities are responsible for the addition of these chemicals into the water. Natural sources such as metal enrich rocks weathering and sediments in the water bodies introduce them to the aquatic systems.

However, it cannot be denied that the natural sources largely depend upon the local geomorphology and hence are less harmful as compared to the anthropogenic sources. The industries dump their wastes into water sources, increasing the amount of heavy metal ions in water sources. The leaching of wastes dumped on the ground and disposal sites adds to the increasing problem of heavy metal ion in water. Besides agricultural run-offs and run-offs from the disposal sites are also the causes of addition of heavy metal ions in wastewater. The contaminated wastewater can easily enter the food chain through various routes and damage the ecosystem (Anawar et al. 2001). Heavy metal ions are highly toxic to the living system because they are non-biodegradable, carcinogenic, and show heavily detrimental effects on the human body. This can create acute to critical toxicity conditions in the human system and may even cause death if not monitored well. The major issues related to the toxicity of heavy metal ions vary from metal-to-metal and each metal shows different effects due to different physicochemical interactions. These interactions may be on the cellular or tissue level of the living organisms. Heavy metal ions can even interact with DNA and lead to the formation of reactive oxygen species (ROS) that can damage the entire genetic system and lead to mutagenesis (Thomas et al. 2021). Heavy metal ions such as lead, zinc, copper and mercury poses a serious threat due to their bioaccumulation and biomagnification in a food chain at various trophic levels. Removal of heavy metal ions is a challenging task for environmentalists because of their highly complexing properties and hence difficult to be dealt with. There are many ways for the removal of heavy metals from the wastewater.

They include some of the conventional techniques such as chemical co-precipitation, ion-exchange, electrochemical treatment, coagulation and flocculation, sedimentation, adsorption and membrane filtration. These methods are decided on the basis of chemical and physical aspects of heavy metals and presence of various interferences. Removal of heavy metal ions is best done through adsorption because of their low cost and easier application methods (Yang et al. 2019). New conventional techniques include the use of porous metal-organic frameworks, which are very effective in the removal of heavy metals. They are well known for their functionalized pores, tuneable surface and various pore structures (Khan et al. 2013). Nanotechnology has impacted the life of human beings and its role in environmental remediation is undaunted and unprecedented. They have a range of applications from electronic devices, biomedical and pharmaceuticals, fuels and energy and many other sectors. Nanomaterials are materials with a particle size ranging from 10 to 100 nm. They are well known for their unique physicochemical properties, such as large surfaces, greater surface–volume ratio and higher selectivity in pollution remediation (ISO 2008). Nanotechnology has strongly impacted environmental issues due to its larger surface area, which provides bigger interaction sites for contaminants. Many nanostructures such as nanosorbents, nanocatalysts and nanofilters have been applied to treat heavy metal pollution.

As discussed above, it is quite evident that heavy metal remediation needs time and deep understanding and attention, especially about the application of nanotechnology for their treatment. To summarize all the above challenges and solution this chapter has been framed in a sequential manner. This chapter has been designed considering various aspects of nanomaterials and their application in the remediation of heavy metal pollution in the wastewater. The chapter will one-by-one unfold the basic aspects like source and health impact of heavy metals and their conventional treatment techniques. As the chapter will progress we will discuss how conventional methods have a limited approach and how nanotechnology has proven its worth. The chapter also covers some of the aspects like limitations of these techniques and what may be the plausible solution for them.

## 10.2 Sources of Heavy Metals and Their Health Impacts

Heavy metals occur in the earth's crust and it is exposed in the environment due to human activities. They cannot be degraded or destroyed by any means and hence become part of persistent environmental contaminants. They enter the human system through food, water and air and can accumulate in the biological system over a period of long time. High concentration of heavy metals can be noted around the area where there are high mining activities or may be due to natural weathering of rocks and bedrock. Mining and metallurgical activities are biggest cause of addition of metal ion impurities in local areas (Madhav et al. 2020). Even those areas where mining activities are shut down, there are cases of addition of pollutants through run-offs and leachates are still going on. Hence, water keeps getting contaminated. Heavy metals are added to water in mining areas in both the forms, i.e. elemental and ionic forms. Some are also added as coordinated complexes (UNEP/GPA 2004). Sometimes metals are by-products and join the wastewater while processing of other elements or compounds. For example, Cadmium is added as a by-product in the extraction of zinc and lead; lead is by-products produced at the exhaust of automobiles; mercury is added during the degassing of the earth's crust. These have classified into categories on the basis of the sources and processes. These have been divided by Ross (1994) into following groups:

- Mining and Metallurgy: This release elements Arsenic, Lead, Cadmium and Mercury during the mining and smelting processes.
- Industrial Sources: Industries such as plastics, paints, petrochemicals, pharmaceuticals and textiles add many metals such as Arsenic, Cadmium, Zinc, Nickel, Copper, Mercury, Cobalt, Chromium, etc.
- Atmospheric Depositions and Meteorological Activities: Rain, storms and asteroids add to the elemental metals in the water bodies. Some of them include Arsenic, Chromium, Copper, Uranium, Mercury and Lead.
- Agricultural activities: Many agro industries and products use metal into their products. Insecticides, Pesticides and Herbicides are source of arsenic, copper, lead, silica, zinc, chromium, etc.
- Waste discharge: Disposal of wastes at home and small sectors are major sources of adding to metal ion in wastewater. Many of the home products use these heavy metals such as mercury, lead, copper, cadmium and zinc.

Sewage and stormwater discharges, incinerations and crematorium, landfills, motor vehicles, smelting, dentists and clinics, research laboratories, scrap yards, metal and treatment units, etc. are varying sources of metal additions into the water sources (Mohammed et al. 2011). Even if we try to disseminate the sources of metal ion addition into the wastewater, we will have multiple examples of the metal ions and their sources. Some of them can be listed as follows (Qasem et al. 2021):

- Lead based batteries used at home, alloys, ammunitions, plastic stabilizers and paints are major source of lead pollution in wastewater.
- Arsenic is added into the ecosystem through electronics and glass production units in their wastewater.
- Brass coatings and cosmetics are major sources of addition of zinc in wastewater. Rubber products also add to this metal.
- Copper is an integral part of the plumbing systems and electronic and cable industries largely include this metal.
- Chromium is a major constituent of the pollutants present in the wastewater in steel and pulp mills. Many tanneries and textile industries use chromium as pigmentation products and hence a bigger threat.
- Batteries, paints and steel industries use cadmium primarily in their processing units. Plastic industries and metal refineries also release large amount of cadmium in their wastewater.
- The electrolytic production of chlorine and industries using caustic soda are major sources of mercury in the ecosystems. Many e-wastes and agricultural wastes leachates and run-offs also add to their problems.

- Steel production units and nickel alloy productions are the major sources of nickel pollution in wastewater.

The problem of heavy metal ions and their health impacts should be considered with utmost care as these pollutants can create trouble for the human system at various levels (UNEP/GPA 2004). They may affect the body at organ, tissue or cellular level based on their interaction mechanisms. Heavy metal cations can easily affect various cell organelles such as cell membrane, mitochondria, endoplasmic reticulum, RNA, DNA and nuclear proteins and cause damage to them. These cellular interactions can create short-term effects or may also create long-term effects based on their structure, chelating behaviour and concentration in the human body. Lead and Cadmium exposure can cause severe damage to kidney and nervous system. Chronic exposure to cadmium can lead to osteoporosis and kidney damages. The toxicity impact of these two metals has emphasized on the production of highly effective nanosorbents. A summarized effect of heavy metals and their human health effects have been listed in Table 10.1.

**Table 10.1** Health effects of some of the heavy metals present in wastewater

| Metal | Acute health effects | Chronic health effects | Permissible limit (µg) | References |
|---|---|---|---|---|
| Arsenic | Nausea, diarrhoea, convulsions, encephalopathy, neuropathy, vomiting | Cancer, lung, skin, hyperpigmentation, diabetes | 10 | Atkovska et al. (2018); Khan et al. (2011) |
| Cadmium | Pneumonitis, damages reproductive systems | Osteomalacia, Lung cancer, Proteinuria | 3 | Atkovska et al. (2018) |
| Chromium | Renal failures, haemolysis | Lung Cancer, Fibrosis Pulmonary | 50 | Atkovska et al. (2018) |
| Copper | Immunotoxic effects and haematological systems, gastric effects. | Brain, kidney, lungs and liver damage | 2000 | Qasem et al. (2021) |
| Lead | Effects on immunity and cardiovascular system | Bones, liver, kidney and brain damage; effects on reproductive system; haematological systems | 10 | Qasem et al. (2021) |
| Mercury | Immunotoxicity, Cardiovascular disorders, Endocrine disruptions | Brain, lungs, kidney, liver, bone degeneration. Reproductive disorders. | 6 | Qasem et al. (2021) |
| Nickel | Gastrointestinal distress, skin issues | Pulmonary fibrosis and kidney damage | 70 | Qasem et al. (2021) |
| Zinc | Stomach Cramps, Skin irritations, Vomiting, Anaemia | Skin diseases, convulsions | 3000 | Qasem et al. (2021) |

## 10.3 Conventional Treatment Technologies

The treatment of wastewater containing heavy metals depends on the problem element and hence need proper analysis before the treatment. The treatment process depends on the ionic state of the metal, electronic configuration and electrode potential. Wastewater from the electroplating units needs highly specialized and effective treatment units for the removal of heavy metals and hence needs proper treatments as well. Similarly other sources of wastewater such as tanneries, agriculture and industrial sectors need proper methods of removal. There are already many techniques that are available conventionally that can assist in the removal of heavy metals from the wastewater. Some of them have been listed below.

### *10.3.1 Adsorption*

The mechanism of adsorption is controlled by the physicochemical behaviour of adsorbents and heavy metals. Other factors that control the adsorption process are temperature, concentration of adsorbent, pH, time and initial concentration of heavy metals. Some of the adsorbents are carbon based such as activated carbon and charcoal because of their large surface area (Singh et al. 2018). Surface modifications of carbonaceous materials can lead to excellent adsorption behaviour and also increase the sensitivity and selectivity of the materials (Thomas et al. 2021). Mineral based adsorbents such as zeolite, clays and silica are found excellent candidates in remediation of heavy metals in wastewater which can be operated at lower costs. Clay based materials shows high cation exchange capacity (CEC), extraordinary selectivity, high surface hydrophilic property, large expansion quality and higher surface electronegativity. The adsorption efficiency of these materials can easily be increased by acid treatment, thermal treatment and pillar bearing. These processes can increase the pore size and volume and specific surface area of the adsorbents (Alshameri et al. 2019).

### *10.3.2 Chemical Co-precipitation and Coagulation-Flocculation*

Chemical co-precipitation techniques are most widely used for the treatment of heavy metals in wastewater. It involves various techniques such as coagulation, flocculation and sedimentation of metal ions using various methods. The heavy metals are chemically precipitated as their sulphates, hydroxides or carbonates in this process. Chemical co-precipitation techniques are highly effective and used because of simple technological systems and cost-effectiveness of application. The effectiveness of this method, however, reduces when there are coordinated compounds of heavy metals. To combat this problem, organic or inorganic precipitants are used. Some of these precipitants are sodium diethyl- and dimethyldithiocarbamate, trimercapto-s-triazine, trisodium salt and sodium trithiocarbonate ($Na_2CS_3$) which are used at industrial scale as well as frequently. They are mostly employed for the industrial wastewater containing Copper, Nickel and Tin widely used in Polychlorinated Biphenyls production units. Other complexing compounds are used with them such as aqueous ammonia, thiourea, EDTA and its sodium salts, trisodium salt of methylglycinediacetic acid and tetra sodium salt of *N*,*N*-dicarboxymethyl glutamic acid when dealing with rare earth elements (Thomas et al. 2021). Coagulation-Flocculation method is employed considering the zeta potential of metals and flocculating agents. The coagulation occurs due to the electrostatic interaction and the particle size keeps on increasing and settling down (Gunatilake 2015).

### *10.3.3 Membrane and Filters*

Membrane filtration is quite famous method in the field of organic pollutant treatments. They can easily remove suspended solids, particles and inorganic contaminants like heavy metals. A membrane filtration process is decided on the basis of particle size under consideration. This may be ultrafiltration (UF), microfiltration or reverse osmosis depending on the conditions of treatments. UF method is applied to separate heavy metals and macromolecules. They can help to achieve almost 90% of the removal efficiency. Polymer supported ultrafiltration helps in the removal of water soluble metal ions through the ligand metal binding process and they have higher efficiency due to selectivity and sensitivity (Gunatilake 2015). A combination of precipitation and ion-exchange is known as complexation-ultrafiltration where water soluble polymers are used as chelating agents and then they form macromolecules. These macromolecules cannot pass through the pores of the membranes and hence trapped (Trivunac and Stevanovic 2006). Reverse osmosis is also well-known method of water purification and has been discussed a lot in many researches.

### *10.3.4 Biological and Electrochemical Remediation*

Electrochemical techniques have been exploited quite a lot for the environmental remediation is undoubting and hence they play an important role in the removal of heavy metal ions from the wastewater. This is done through direct electrolysis, electro dialysis or ion-exchange methods. However, these are limited in applications because of the unavailability of cheaper and less reactive electrode materials and higher sensitivity towards the change in pH. The charge per molecule for the organic species used in electrolysis limits the application of electrochemical removal of heavy metals (Janssen and Koene 2002). Bioelectrochemical systems have been used for the treatment of metal ions in polluted water. They have microbial consortium at the anodic end and much robust in nature. Microbial fuel cells (MFC) and Microbial Electrolysis Cell (MEC) have been studied extensively for the treatment of pollutants and even for the metal ions. Biocatalytic and electrochemical reduction of heavy metals occurs at the cathodic chamber of these electrochemical cells. They have been studied for the removal of toxic metal ions from the aqueous systems (Pb, Cd and Ni). They are robust systems with reduction in the generation of power and enhanced uptake of the metal ions as well as microbial products degradation (Chakraborty et al. 2020). Bacterial strain resistant extracts bio-films have been used for the removal of mercury in wastewater. The experiment has been performed in the column over the laboratory conditions and it was found that mercury ions were reduced to metallic mercury. The mercury containing sample was taken from the wastewater of chloralkali industries in Europe and bacterial strain of *Pseudomonas putida Spi3* (Canstein et al. 1999).

## 10.4 Application of Nanomaterials

Nanomaterials have been synthesized and designed in the environmental remediation techniques just to overcome the limitations that have been faced in the conventional treatment approaches. The larger surface area of nanomaterials makes them an effective remedial tool for heavy metal remediation for the wastewater. They have higher interaction with the pollutants that can increase their efficiency for the removal of heavy metals and therefore, they are highly preferable over the conventional treatment techniques. Many of the nanostructures such as nanoadsorbents (nano-silica, nano-zinc oxide), nanomembranes (MWCNTs, SWCNTs, modified graphene) and polymer nanocomposites have been used in the treatment of heavy metal ions. These methods are highly efficient in terms of their cost-effectiveness, removal efficacy and easier recycling and regeneration of the reactive surfaces. Each nanomaterial holds its own unique property which will be discussed under various remediation methods in the following sections.

### *10.4.1 Adsorption Treatment*

Nanomaterials are well known for their adsorption based applications because of their larger surface area and surface chemistry of them are easily tuneable and tailored. These nanoadsorbents can easily adsorb many toxic substances including heavy metals. The mechanism of action can be through ion-precipitation, ion-exchange and simple physisorption. On the addition of nanoadsorbents into the wastewater containing heavy metals there is diffusion of heavy metals on the outer surface of the materials. This is due to diffusion potential gradient which is generated between the heavy metal and surface of the nanosorbents. Once the diffusion is complete the heavy metals travels into the pores of the adsorbents. The process of adsorption may be either physisorption or chemisorption depending upon the charge of metal and surface. However, there is slightly different mechanism when it comes to polymer-based adsorbents. The mechanism that follows in such nanomaterials is either complex formation or electrostatic interactions. Nanoadsorbents are broadly divided into three classes: carbon-based, polymer nanocomposites and metal and metal oxides depending on their basic nanostructure constituents (Lata and Samadder 2016). Focus has been made on composites based materials for higher efficiency, more surface modifications and much effective removal of heavy metal from the wastewater.

Carbon nanotubes (CNTs) are well-known nanoadsorbents that are applied in the removal of heavy metals from the water when they are present in their oxidized form. This is mainly due to the fast kinetics. These nanotubes can remove metal ions from water through physical adsorption, sorption–precipitation mechanism and electrostatic interaction or may be through chemical adsorption processes. Some of the time there may be two or more than two mechanisms that are responsible for the adsorption processes. The CNTs can easily be modified on their surface either through acid treatment techniques or grafting methods. Acid treatment method is applied for the introduction of various functional groups on their surfaces. The introduction of functional groups increases the absorption capacity of the CNTs. The metals ions ate adsorbed on the surface of these nanostructures and then promote the exit of $H^+$ from surface and hence the pH of water is lowered (Ihsanullah et al. 2016). They are found highly effective in the removal of metal ions such as Mn(VII), Pb(II), Cu(II), Cr(VI), etc. (Yadav and Srivastava 2017). Phenol, hydroxyl and carboxyl are some functional groups that control the surface properties of modified CNTs. Graphene oxide is another carbon-based nanomaterial that has been applied for the removal of heavy metal ions (Mukherjee et al. 2016). A magnetic hydroxypropyl chitosan/oxidized multiwalled carbon nanotubes (MHC/OMCNTs) nanocomposite has been synthesized and used for the adsorption of lead ions. The overall adsorption followed pseudo-second order kinetics and material was highly effective for the removal of lead ions (Wang et al. 2015). The summarized form of such adsorption has been explained in Fig. 10.1.

Metal-based nanomaterials are very famous method for the removal of heavy metals. They are easy to synthesis, low cost, have high adsorption capacity and easy to regenerate. Nano-oxides such as Zinc oxide, Titania, iron oxides, aluminium oxides, copper oxides, nickel oxide and ceria are well-known metal oxides that are applied in the treatment. As the size of metal oxide nanoparticles decreases the adsorption efficiency of the nanomaterial increases. Nanocarbons that are impregnated with the metal oxides have been found to be excellent adsorbents of heavy metals. The metal oxide nanoparticles can easily be regenerated through the acid treatment and their efficiency stays even after much regeneration (Qu et al. 2013). Bimetal oxides like Fe-Mn, Fe-Cu, Ce-Ti, Mn-Al, etc. are used as an adsorbent for the metal ions. These bimetallic oxides have higher capacity of adsorption than their individual nano-oxides. For example, the arsenic adsorption capacity of Fe-Mn oxide is much higher (20–50 times) than Iron or Manganese oxides. Bimetallic

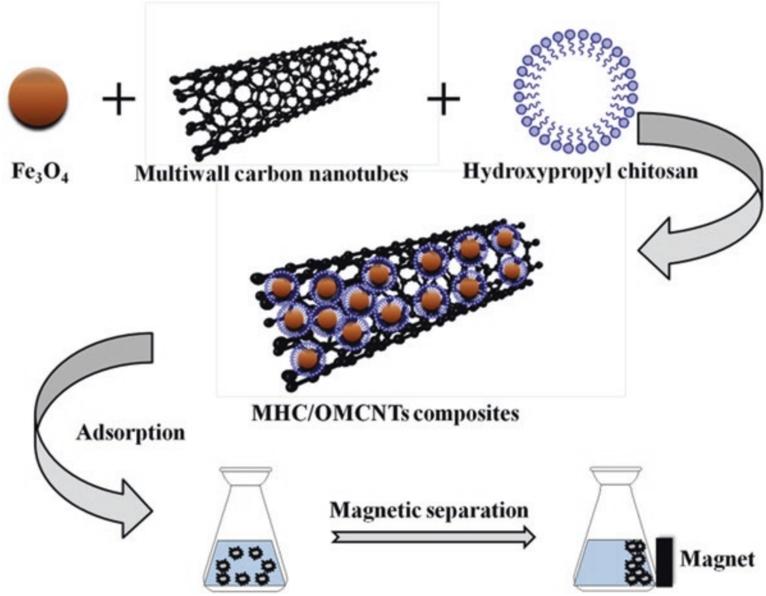

**Fig. 10.1** MHC/OMCNTs composite for removal of lead ions. (Copyright Reserved Elsevier, 2015. Reprint Permission taken)

oxides can be synthesized through hydrolysis and precipitation or grinding mechanisms (Parvin et al. 2019). Composites of Iron oxide in macroporous silica ($Fe_x$MOSF) are an excellent adsorbent for the removal of arsenic from the wastewater. Lead and cadmium removal has been effectively done with metal oxides such as Alumina, Ceria and Titania nanoparticles. ZnO and NiO nanoparticles have efficacy in the removal of these metals even at the acidic conditions. Even the activities of NiO nanoparticles were found to be higher towards Pb(II) as compared to Cd(II) (Sheela and Nayaka 2012). Titanate nanoflowers were synthesized and applied in the removal of highly toxic contaminants from the wastewater. This material was found to be highly effective in the treatment of Zn(II) and Ni(II) (Huang et al. 2012). The use of polymer-based nanocomposites, where nanoparticles are impregnated in the polymer agglomerates are quite popular these days as nanosorbents. The metal ions form chelates with the surface functional groups of the polymers. These nanocomposites are synthesized by the encapsulation methods where metal nanoparticles are captured in the polymer matrix during the polymerization. One of the best examples for this is ZVI-NP imbedded on a resin support (Kenawy et al. 2018).

### 10.4.2 Magnetic Removal

Magnetic adsorbents are materials that host iron oxide nanoparticles ($Fe_3O_4$) which have proven to be excellent in treatment of copper and other magnetically active metal ions. These nanomaterials can be comprised of the base structures of carbon, polymers, modified starch or any kind of biomasses. The adsorption processes are mostly controlled by factors such as magnetic field, surface charge density and redox properties of the metal ions under study. They are well known for their easy synthesis routes, extraordinary surface charge behaviour and recyclability and reusability. Common nano-level magnetic adsorbents used for the removal of heavy metal from the wastewater are zero-valent iron nanoparticles (ZVI-NP), oxides of iron such as haematite ($\alpha$-$Fe_2O_3$), maghemite ($\gamma$-$Fe_2O_3$) and magnetite ($Fe_3O_4$) and some of the spinel ferrites. The adsorption and removal processes depend upon surface morphology and magnetic behaviour of the nanomaterials. Iron oxide nanoparticles have been found to be of great benefit in the removal of arsenic based ions from the wastewater. Cellulose matrix loaded with ferric oxide and β-Cyclodextrin (CMβCD)-monodisperse magnetite nanoparticles were reported to be effective in the removal of As(III) and As(V) (Dave and Chopda 2014). Amine functionalized Silica coating $Fe_3O_4$ nanoparticles has been found effective in the removal of Cu(II) from the wastewater with 98% efficiency. The amine functional group increases the functionality of adsorbent with increasing pH and hence suitable for high pH conditions (Hua et al. 2012). The $Fe_3O_4$-polyvinyl acetate-iminodiacetic acid is an EDTA containing nanomaterials and it was also an excellent magnetic adsorbent for removal of Cu(II) (Tseng et al. 2009). $Fe_3O_4$ magnetic nanoparticles were surface modified with APTES (3-aminopropyltriethoxysilane) and co-polymers of Crotonic and Acrylic acid for the removal of heavy metal ions Cd(II), Zn(II), Pb(II) and Cu(II) from their solutions. They showed excellent results at pH 5.5 and were easily recyclable as shown in Fig. 10.2 (Li et al., 2013). The functionalization of magnetic nanoparticles reduced the agglomeration and hence they showed more active sites for the binding of metal ions. Organosilanes are lesser in toxicity and also more biocompatible hence used in functionalization (Ge et al. 2012).

Another magnetic nanoparticle of $Fe_3O_4$ which was stabilized by two non-ionic and one cationic surfactant was synthesized using co-precipitation methods. These surfactants were based on *p*-phenylenediamine and non-ionic surfactants were ethoxylated para phenylenediamine tetraoleate with 45 and 55 ethylene oxide units and the cationic surfactant was ethoxylated para phenylenediamine di decane ammonium bromide with 55 ethylene oxide units. These surfactants stabilized the nanoparticles and they have been found to be effective in the removal of Pb(II), Cd(II) and Zn(II) (El-Dib et al. 2020). Poly(1-vinylimidazole) with a trimethoxysilyl terminal group grafted on magnetic nanoparticles of maghemite was used for the removal of Cu(II) ions from the aqueous solution (Takafuji et al. 2004). Another magnetic nanoparticle of iron oxide was grafted with polyglycerol and was analysed for the removal of heavy metals from secondary effluent industrial wastewater.

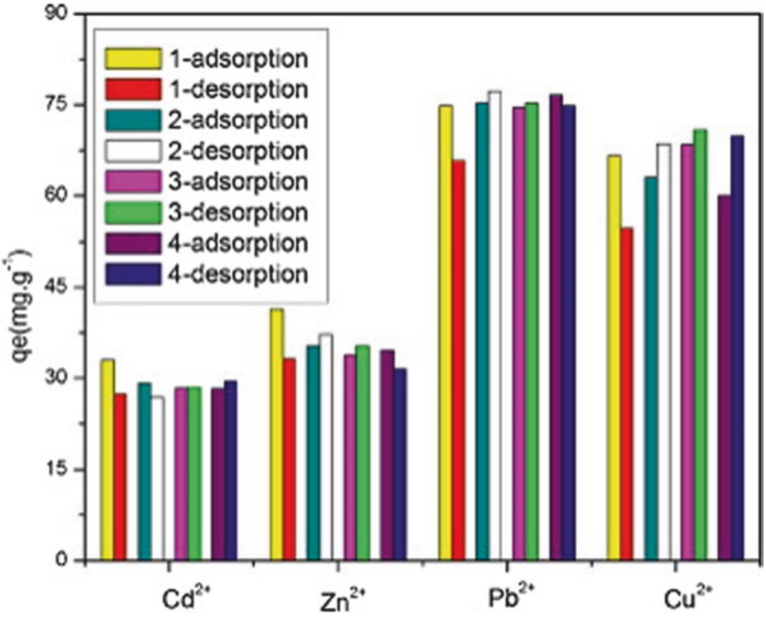

**Fig. 10.2** The performance of $Fe_3O_4$@APS@AA-co-CA by multiple regeneration cycles. (Copyright Reserved Elsevier)

The materials removed Ni, Cu and Al from the wastewater quite effectively. The adsorption kinetics of these nanoparticles followed pseudo-second order along with the intra-particle diffusion of metal ions (Almomani et al. 2020).

### *10.4.3 Nanomembranes and Nanofilters*

Membrane filters are one of the most popular and reliable techniques for the removal of heavy metal ions from the wastewater. But fouling stands as one of the major hurdles when it comes to membrane-based treatment technologies. It reduces the water permeation flux and water quality. It also leads an increase in the energy consumption. Fouling of the membranes can be due to blocking of the pores, adsorption of some organic molecules, inorganic precipitations or accumulation of biological substances which reduces the flux density and hence decreases the treatment efficiency. Hence antifouling membranes have become the need of the time. Electroactive antifouling membranes are solution to this issue. In these membranes, there are modifications which are done using a conductor nanomaterial such as Titania nanoparticle or PANI nanopolymers. Other antifouling membranes involve CNTs. The overlapping and reticular features of these CNTs are useful in designing highly interconnected and densely porous membranes for the removal of heavy metals (Liu et al. 2020). Liu et al. (2021) developed a Sea urchin-like FeOOH functionalized CNT nanofilter that has been found to be highly effective and faster removal of arsenic through arsenite decomposition. This material was prepared via electrodeposition technique and one-step decontamination of As(III) has been achieved through it. The system was highly adaptive towards various pH conditions and environmental matrices. This CNT-FeOOH nanofilter was found to be highly regenerative and it can be simple chemically washed and cleaned. The application of nanocomposite electrospun fibre membranes having sorptive properties have been investigated for the removal of heavy metal ions has been done. One of them is electrospun fibre membrane which was doped with nano-boehmite (hydrated alumina or alumina hydroxide, AlOOH). The nano-boehmite was incorporated to increase the surface area of the active nanocomponent. Hydrophobic/PCL/and hydrophilic/Nylon-6/ were the polymers that were chosen as the support for the boehmite. This material has been used as membrane for the removal of Cadmium ions in the aqueous solution (Hota et al. 2008). Electrospinning generates ultra-fine fibres uniformly and also produces submicron fibres for higher efficiency. Dual-layer polybenzimidazole/polyethersulfone (PBI/PES) nanofiltration (NF) hollow nanomembranes have been designed for the removal of heavy metal ions from the wastewater. The target metal ions were Cd(II), Chromate and Pb(II). The membrane has been developed through co-exstrusive fabrication of polybenzimidazole and polyethersulphone/polyvinylpyrrolidone. These have been fabricated through a triple-orifice spinneret and Polybenzimidazole was chosen as the outermost layer because of its higher chemical resistance and unique charge properties. The use of polyethersulphone/polyvinylpyrrolidone has been done as a supporting layer because of lower cost, higher mechanical strength, super spinning power, hydrophilicity and easier synthesis of pores in the membrane systems. The material showed high removal efficiency for Cd(II) and Pb(II) and highest for Chromate ions (Zhu et al. 2014). Mesoporous silica is an excellent adsorbent which is widely discussed in field of metal ion removal from wastewater. Mesoporous silica (m-$SiO_2$) on MWCNTs where silica surface has been modified using (amino-ethylamino)-propyltrimethoxysilane applied as nanofilter for the removal of heavy metals. This material holds the dual benefit of mesoporous silica and MWCNT, i.e. high mechanical strength, larger surface to volume ratio, layered structures, chemical stability and thermal resistance. This material was found to be highly effective in the removal of Cu(II) through adsorption and chelation of Cu(II) by the amine groups on the silica surface. A schematic representation is given in Fig. 10.3 for an explanatory outlook (Yang et al. 2013).

A loose nanofiltration hybrid membrane was designed through the self-assembling of ethylenediamine (ED) which has been grafted over MWCNT to form ED-g-MWCNT. This assembling was done on the topmost layer of Polyethersulphone (PES) asymmetrically. This assembling has been done using non-solvent induced phase separation (NIPS) process. This material showed enhanced thermal stability, chemical inertness and mechanical strength as compared to pure PES membranes. The Donnan exclusion and steric hindrances promoted the removal of metal ion through the rejection processes (Peydayesh et al. 2020). Similarly, polyacrylic acid functionalized cellulose nanofibres membranes which have been modified with

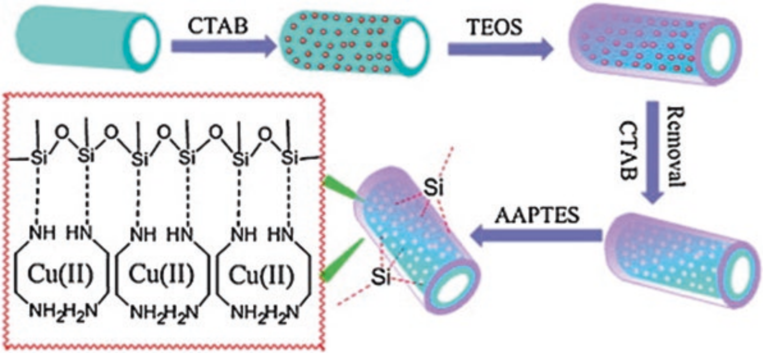

**Fig. 10.3** The synthetic route to NN-m$SiO_2$@MWCNTs. (Copyrights reserved Elsevier 2013)

poly(glycidyl methacrylate) have been used for the treatment of heavy metals and they have been used in the ion-exchange removal of Cadmium (Chitpong and Husson 2017). Zeolite nanoparticle impregnated polysulfone (PSf) membrane has been designed for the removal of lead and nickel from the wastewater (Yurekli 2016). There are many such examples of membrane-based systems.

### 10.4.4 *Electrochemical Nanomaterials*

The electrochemical properties of CNTs can be used for the electrochemical-assisted filtration of wastewater with simultaneous induction of redox reaction and detoxification of heavy metals ions while passing through them. An electrochemical system of Titania-CNT has been developed for the removal of Antimony (Sb(III)) using Titania as cathode and nanocomposite with CNT as anode. On the application of electric field, the highly toxic trivalent species of Antimony oxidizes to less toxic Sb(V). The entire detoxification process is controlled through the change in voltage and highly effective for the treatment of antimony pollution. This method is more like "oxidation-sorption" technique for the removal of metal ions. The performance of these electrochemical systems can easily be tuned and enhanced with the replacement of Titania nanoparticles with more Sb specific nanosorbents. This may be either titanate nanowires or oxides of iron. Introduction of MOFs in such systems may create photoelectrochemical synergistic effects. MIL-88B(Fe) photocatalysts are one such example that has boosted efficiency for the removal of Sb(III) (Liu et al. 2020). Another application of nanoelectrochemistry for the treatment of heavy metal ion is "reduction-sorption" with Cr(VI) as the target metal ion. As it is well known that Cr(III) is 1000 times less toxic as compared to its hexavalent species, electrochemical CNT-PANI system was developed. The amine and imine functional groups of PANI (Polyaniline) can easily capture Chromium ions due to their chelating behaviour and application of suitable voltage can change the oxidation state of the metal. The increase in the flow rate and voltage increases the detoxification process. A similar system of PVA-CNT was also developed for the reduction and treatment of Chromium(VI). The electrostatic forces in these systems prevent the flow of chromium ions under lower salinity. These methods are cheaper and highly promising when it comes to removal of metal ions from wastewater (Duan et al. 2017).

## 10.5 Limitations and Plausible Solution

Nanomaterials, even though have proved their strong role in the field of heavy metal remediation, many points are still unnoticed or over looked. These points need to be addressed for a larger and safer application purpose. Some of these limitations and plausible suggestions have been made in the points below (Yang et al. 2019):

- The first and the most important point that need to be addressed is the stability of nanomaterials as they tend to aggregate and hence the removal capacity of them is highly reduced. This destroys the basic purpose of nanomaterial applications. Their removal from the aqueous solution sometimes becomes too tough because of their size in nano-scale. Most of metal oxides nanoparticles used as adsorbents of heavy metals show tendency of agglomeration and hence their polymer-based nanocomposites prove to be beneficial in this regard. The synthesis of nanoparticles and polymers together incorporates the nanoparticles within the polymer matrix and prevent the agglomeration of metal oxide nanoparticles.
- Highly effective nanomaterials are difficult to synthesize and their industrial scale application needs more study and investigation. There is need to develop market-available nanomaterials that can be easily accessed and exploited for the remediation of wastewater contaminated with heavy metals. The other problem that stays with the easily available nanomaterials is their limited study in relation to the toxicity effects. There is a limited data available for the biocompatibility for most of the nanomaterials.
- Synthesis of nanomaterials from their precursors is a chemical process and each process adds to the new pollutants in the system. This can kill the entire zest of environmental protection as we keep on adding wastes from the other side. So it must be ensured that we develop such systems which are easier to synthesize and recyclable such as magnetic nanomaterials. Employing natural resources as a precursor of nanomaterials is another best way to restore the idea of sustainability.
- GO, even though show high effectiveness in the removal of heavy metal ions from the wastewater, poses a severe threat of leaching out of GO nanoparticles. The cost of production graphene and its oxide is very high. This can only be lowered through the impregnation of GO on a mixed matrix membrane system. Other problem that is related to CNTs is the difficulty in separation after treat-

ment. The toxicological studies of CNTs are also going on and needs special attentions.

These are some suggestions that may be considered by the researchers for more efficiency and reduced waste generation for the treatment of heavy metal contaminated wastewater.

## 10.6 Conclusion

Water pollution with the time has become a grave situation for the existence of human race. While all of us depend on water for our survival we cannot undermine the limitedness of these natural resources. We have seen various natural and anthropogenic sources that are polluting water especially heavy metal in wastewater. The presence of metal in water may cause many serious health conditions ranging from minor conditions such as itching, cramps and rashes to acute situations such as cardiovascular disorders and gastrointestinal infections and may reach a chronic condition like kidney, heart, liver or lung damage. The heavy metal pollution water needs proper monitoring and remediation. As we have discussed about the conventional treatment techniques such as adsorption, chemical co-precipitation, ultrafiltration, electrochemical treatment and other methods we have found that each method has its own pros and cons. The problems that were related with conventional techniques had been dealt with the application of nanomaterials. Nanomaterials, which show highly tuneable properties and functions with higher mechanical strength, surface area and chemical and thermal stability, have been employed in the treatment of heavy metal in wastewater. Metal oxides, carbon nanotubes, mesoporous silicate frameworks, metal-organic frameworks and polymer nanocomposites have proved their excellent behaviour in the field of heavy metal ion remediation. Nanomaterials have been exploited widely in the heavy metal treatment due to their outstanding properties. Carbon nanotubes have large surface-volume ratio and the surface of material can be functionalized with phenolic, carboxylic and hydroxyl groups for the effective removal of metal ions from the water. They have been used as adsorbents, nanofilters, nanomembranes and electrochemically designed for the rejection of metal ions. Mesoporous silica structures are a wide topic for study as they have high chemical and thermal stability and easily tuneable surface properties.

This surface of silicate frameworks can easily be functionalized by amines, carboxyls, hydroxy and Schiff bases for effective removal of metal ions from wastewater. The surface of mesoporous silica can even be tuned in a way where it can go for selective treatment of contamination. Many works have focussed on the development of mesoporous Silica and CNT frameworks to have more efficient system of treatment. Magnetic nanomaterials are highly advanced treatment methods which preferably employs iron oxide based nanostructures for the removal of metal ions. They are easier to synthesis, cost-effective and can be easily removed after operating. The best part of these materials lies in their easy regeneration and recycling with good efficiency rate in every cycle. Nanofilters and nanomembranes have also contributed a lot in the field of water treatment and they have helped in overcoming many untouched problems of conventional membranes such as fouling of the surface and hence proved their worth. Electrochemical application of nanomaterials in the field of treatment of heavy metals has also been discussed and we can see there are many new features that have been introduced in past 2–3 years which has helped in increasing the efficiency of the cleaning processing. Every technology, however, comes with certain limitations, hence we need possible solutions and problems that are attached to these treatment techniques. Some of the under looked problems that are associated with these nanomaterials are nanotoxicity which is still limited in investigation terms and hence it needs a detailed insight and study before applying on a large scale.

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# Chapter 11
# Agricultural Residue-Derived Sustainable Nanoadsorbents for Wastewater Treatment

**Karuna Jain, Pooja Rani, Manvendra Patel, Sarita Dhaka, Saurabh Ahalawat, Anuj Rana, Dinesh Mohan, Krishna Pal Singh, and Rahul Kumar Dhaka**

**Abstract** Water resources are getting contaminated globally in a very fast manner due to natural and anthropogenic practices. If this happens with such a pace, it will lead to freshwater scarcity. Therefore, economically feasible, easy to use and technically simple technologies for water treatment must be developed proactively. Adsorption technique, among the other water treatment technologies, might be favorable for the said purpose in terms of techno-economic aspects (cheap, universal, and eco-friendly). However, conventional adsorbents like clay, silica gel, activated carbon, limestone, and activated alumina have certain inherent issues which

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make their real-world application limited. Therefore, emerging nanoadsorbents may be employed as a replacement of conventional adsorbents in wastewater treatment. Nanoadsorbents have high surface area, porosity, and tunable characteristics. The challenges with the application of nanoadsorbents for wastewater treatment include identification of low-cost and sustainable adsorbent precursor materials. The agricultural residue-derived nanoadsorbents have a potential to deal with the above challenges. A variety of agricultural residue-derived adsorbents such as nanosilica, nanocellulose, nanobiochar and their composites have been developed and used for wastewater treatment. This chapter gives an overview of the available wastewater treatment technologies and covers the development and application of agricultural residue-derived nanoadsorbents for wastewater treatment including the concepts like operating mechanism, regeneration and selection of adsorbents. Chapter ends with the conclusions and potential recommendations.

**Keywords** Wastewater treatment · Agricultural residue · Adsorbents · Nanotechnology · Nanobiochar · Emerging pollutants

## 11.1 Introduction

Industrialization and rapid population growth have polluted water resources globally and caused a challenge of freshwater availability. This is particularly important when the demand of freshwater doubles every two decades. Approximately 40% of the global population (from 80 countries) is facing water deficiency. About 500 billion m$^3$ fresh water is used by industries every year (Ali et al. 2021). Industries such as fertilizer, paper and pulp, steel, sugar, textile, thermal power plant, etc. contribute majorly towards water pollution. Water resources are being polluted due to unwanted entry of various pollutants.

Pollutants may basically be classified as conventional and/or emerging pollutants. Conventional pollutants include fluoride, nitrate, and trace metals while emerging pollutants comprise but not limited to steroid, hormones, pharmaceuticals and personal care products, artificial sweeteners, surfactants (Ahamad et al. 2020), antibiotics, sunscreens (Caliman and Gavrilescu 2009), naturally occurring algal toxins, steroids, endocrine disruptors and their degradation intermediates (Preda et al. 2012), gasoline additives, fire retardants, plasticizers, and microplastics (Browne et al. 2015). Emerging pollutants are present in trace amount (ng/L–μg/L), but their long persistence in the environment significantly affects water quality, health of human and animals and ecosystem. Further, pollutants may be classified as inorganic, organic and biological in nature. A constant flux of heavy metals and other inorganics originated from industrial and municipal wastewater, mine drainage is contaminating surface waters and sediments (Hoque and Philip 2011). Organic pollutants include fertilizers, plasticizers, polybrominated biphenyls, phenols, detergents, greases, formaldehydes, oils, hydrocarbons, pharmaceuticals, and pesticides (fungicides, herbicides, insecticides) (Ali et al. 2012). Major sources of organic pollutants are chemical and agricultural industries. Bacteria, viruses, fungi, algae, and amoeba are the examples of biological pollutants which affect human health and may cause nausea, rheumatoid arthritis, kidney damage, chronic diseases, circulatory system, and nervous disorders (Ali 2012).

Monitoring of emerging pollutants is difficult due to their low concentration but advanced separation techniques (liquid-liquid extraction, polymer grafted matrix, magnetic nanoparticles based solid phase extraction) (Moliner-Martínez et al. 2011) and analytical techniques (GS-MS, LC-MS, LC-MS-MS) (Hernández et al. 2007), capillary electrophoresis (Moliner-Martínez et al. 2011) are capable of detecting emerging pollutants even at trace level. Efficient, selective and cost-effective wastewater treatment techniques are necessary to develop in the above scenario. Available wastewater treatment methods are filtration (Barakat 2011), precipitation (Fu and Wang 2011), ion exchange (Kurniawan et al. 2006; Peng and Guo 2020), advanced oxidation processes (García-Montaño et al. 2006; Dhaka et al. 2017), biological treatment (Aksu 2005), reverse osmosis, distillation, electrochemical dialysis (Gunatilake 2015), and adsorption (Kwon et al. 2016; Patel et al. 2019, 2021; Kumar et al. 2020). The process of wastewater treatment is becoming expensive regularly as the prescribed standards for discharge are getting more and more stringent.

Adsorption is one of the prominent wastewater treatment techniques due to low operational and maintenance cost and ease of operation (Gupta et al. 2012; Singh et al. 2018). The efficiency of adsorbents depends upon its specific surface area, pore volume, and available binding sites (Hassan and Carr 2021). A number of conventional adsorbents, namely activated carbon, silica gel, clays, limestone, chitosan, and zeolites are used for wastewater treatment (Krstić et al. 2018). Different pollutants like dyes (Muhd Julkapli et al. 2014), heavy metals, metalloids, pesticides, and pharmaceuticals (Patel et al. 2019) have been removed using adsorption process (Dawood and Sen 2014; Singh et al. 2018; Rathi and Kumar 2021).

Conventional adsorbents have issues like their high cost, low removal efficiency, fast exhaustion, and poor regeneration capacity. The performance of adsorbent may be improved via surface modification, composite preparation among the several other routes. The complex and multistep processes for modifications are either expensive or less feasible for large-scale production (Bhatnagar et al. 2013). To overcome these limitations, nanoadsorbents can be used for wastewater treatment (El-Sayed 2020). Nanoadsorbents have relatively high chemical reactivity, conductivity, large surface area, and specificity making them a preferred choice over the conventional adsorbents (El-Sayed 2020). Nanoadsorbents may be prepared through sol-gel, sono-chemical, mechanical, microwave, and chemical process (Rangari et al. 2017; Biswas et al. 2019). The use of nanoadsorbents for wastewater treatment is a win-win strategy as they can be developed using agricultural residue. Further, agricultural residue burning is a serious problem in certain areas of India; it causes loss to soil health, unbearable air pollution and the health affects. Therefore, converting this agri-waste into nano-adsorbents is a “double-edged sword” with benefits of solid waste management and wastewater treatment.

This chapter gives an overview of various wastewater treatment techniques and emphasizes over sorptive removal of pollutants from wastewater using agriculture residue-based nanoadsorbents. Efficiency of nanoadsorbents over conventional adsorbents has been discussed. Silica, cellulose, lignin, and biochar-based nanoadsorbents are being included in the discussion.

## 11.2 Available Wastewater Treatment Techniques

Wastewater treatment includes primary, secondary, and tertiary stages (Fig. 11.1). Primary stage includes physical processes such as screening, grit removal, and sedimentation. Secondary stage comprises biological treatment, namely aerobic, anaerobic digestion, activated sludge treatment, trickling filtration among the other process. The tertiary stage mostly includes chemical treatment of wastewater. This stage is the most important as, at this stage, toxic and harmful pollutants are converted into less toxic forms or eliminated to meet the accepted standards. These wastewater treatment stages should be collectively used to achieve better results (Gupta et al. 2012). A brief overview of the wastewater treatment techniques has been provided in the following paragraph and summarized in Table 11.1.

The screening includes filtration (i.e., removal of coarse solids) via slow sand filtration (Verma et al. 2017) is a primary wastewater treatment technique which eliminates commonly present conventional suspended pollutants from wastewater (Barakat 2011). Biological filtration (Aziz and Ali 2016), a secondary stage process, is the bacteria-derived degradation of ammonia to nitrites and eventually to less toxic nitrates. Membrane filtration techniques such as microfiltration, nanofiltration, ultrafiltration and reverse osmosis, fall under tertiary stage of wastewater treatment, are used to remove pollutants according to their particle size (Zazouli and Kalankesh 2017). Microfiltration and ultrafiltration using ceramic membranes have been reported to remove chemical oxygen demand (COD) (>87%), color (>96%),

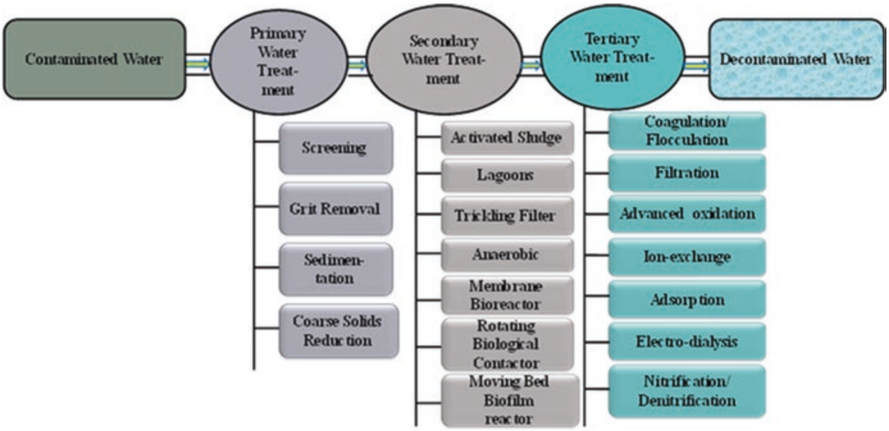

**Fig. 11.1** Wastewater treatment stages

**Table 11.1** A comparative evaluation of wastewater treatment processes

| S. No. | Treatment processes | Advantages | Disadvantages | Cost (US$ per million L) | References |
|---|---|---|---|---|---|
| 1. | Adsorption | Low operation and maintenance cost, simple design, easy to operate, efficient regeneration of adsorbents, broad spectrum of pollutants are removed | Chemical modification of adsorbent is required to increase adsorption capacity<br>Loaded adsorbent may be considered as hazardous material | 10–200 | Ali and Gupta (2006), Singh et al. (2018), Patel et al. (2019) |
| 2. | Advanced oxidation processes | Efficient, quick to degrade organic pollutants | Undesirable toxic compounds may be produced<br>High operational and maintenance cost | 100–2000 | Gupta et al. (2012), Crini and Lichtfouse (2019) |
| 3. | Biological treatment | Reduce BOD, COD, and removes organic and inorganic pollutants, potential energy resource | Slow process<br>Provides environment to grow microorganisms<br>Limited operation flexibility<br>Requires larger space | 20–200 | Gupta et al. (2012), Ali et al. (2020) |
| 4. | Chemical precipitation | Non-selective, easy to operate | High sludge generation<br>High maintenance cost | 20–500 | Kurniawan et al. (2006), Gupta et al. (2012) |
| 5. | Coagulation-flocculation | Sludge settling capability, dewatering capability, bacterial inactivation ability | Large amount of chemicals required<br>Large sludge generation | 25–500 | Leiknes (2009), Gupta et al. (2012) |
| 6. | Electrodialysis | Selectivity towards pollutant removal | High energy consumption<br>Membrane fouling<br>High operational and maintenance cost | 15–400 | Gupta et al. (2012), Ali et al. (2020) |

(continued)

**Table 11.1** (continued)

| S. No. | Treatment processes | Advantages | Disadvantages | Cost (US$ per million L) | References |
|---|---|---|---|---|---|
| 7. | Ion exchange | High regeneration, highly selective for pollutants removal, no sorbent loss | Not effective for non-ionic pollutants (disperse dyes) | 50–200 | Gupta et al. (2012), Crini and Lichtfouse (2019) |
| 8. | Membrane filtration | High removal efficiency, additives free, less chemical consumption, small space required | Limited flow rate<br>Membrane clogging<br>High capital cost<br>High maintenance cost | 15–400 | Qin et al. (2002), Gupta et al. (2012) |

total suspended solids (TSS) (~100%), and turbidity from anaerobically treated dairy wastewater (Zielińska and Galik 2017).

In case of chemical precipitation, precipitant reacts with dissolved metal ions in wastewater and converts into insoluble sludge followed by its removal via sedimentation or filtration (Zamboulis et al. 2004; Fu and Wang 2011). Precipitant like lime, limestone, alum, sodium hydrogen carbonate, and ferric chloride are used for wastewater treatment (Gupta et al. 2012). The precipitant (for example, limestone) has been reported to remove more than 90% of $Cd^{2+}$ and $Cu^{2+}$ from water ($p$H 8.5) (Aziz et al. 2008).

$$M^{n+}(aq) + nOH^{-}(aq) \leftrightarrow M(OH)_n \downarrow$$

Ion exchange process uses an ion exchange membrane which potentially eliminates colloidal and soluble ionic contaminants from wastewater (Kurniawan et al. 2006). The anion exchange membrane retains the anions and rejects cations. However, the cation exchange membrane retains cations and rejects anions (Barakat 2011). A combined anion and cation exchange membrane efficiently removes dissolved organic carbon (76%) and total hardness (97%) using NaCl regeneration solution (20%) (Comstock and Boyer 2014).

In case of biological methods of wastewater treatment, microbes are used to decompose organic pollutants especially emerging pollutants from water into simpler non-toxic compounds under controlled temperature and physicochemical conditions (Aksu 2005). Microbial action in the absence of oxygen to degrade organic matter from wastewater is known as anaerobic biological wastewater treatment (Eq. 11.1) (Mohan et al. 2007). Aerobic microbes (bacteria and fungi) decompose organic contaminants in wastewater in the presence of oxygen (Eq. 11.2). Aerobic digestion of enzyme pre-treated biosolids has been reported to remove emerging pollutants from wastewater collected from local municipal wastewater treatment plant (up to 90%) (Vaithyanathan et al. 2021). Cassava starch wastewater was treated using an up-flow multistage anaerobic reactor and 87.9% COD was removed within 6 h of hydraulic retention time (Sun et al. 2012).

$$\begin{aligned}&\text{Organic matter} + \text{Anaerobic bacteria} \rightarrow CO_2 + H_2O \\ &\quad + \text{Co-products} + \text{Anaerobic bacteria}\end{aligned} \tag{11.1}$$

$$\begin{aligned}&\text{Organic matter} + O_2 + \text{Aerobic bacteria } CO_2 + \\ &\quad H_2O + \text{Co-products} + \text{Aerobic bacteria}\end{aligned} \tag{11.2}$$

The wastewater treatment using oxidation process involves decomposition of organic contaminants into simpler compounds like aldehydes, carboxylates, and sulfates (Garcia-Segura et al. 2013). Numerous oxidants like chlorine ($Cl_2$), hydrogen peroxide ($H_2O_2$), Fenton catalyst ($H_2O_2$ + Fe(II)), Fenton like catalyst and ozone ($O_3$) may be used as oxidants in wastewater treatment (Saputra et al. 2011). However, when single oxidation technique is not sufficient for complete decomposition of organic pollutants, two or more oxidation techniques might be used simultaneously to generate reactive radical species such as hydroxyl free radical and sulfate radical anion which degrade organic pollutants in wastewater. This technique is known as advanced oxidation process (AOP) for wastewater treatment (García-Montaño et al. 2006). Nanoscale zerovalent iron (nZVI) impregnated biochar (BC) composite (a Fenton like heterogeneous catalyst) was prepared. The nanobiochar (nZVI to BC (1:5)) successfully degraded trichloroethylene via Fe(II)/Fe(III) redox and electron-transfer reaction pathways in aqueous solutions (Yan et al. 2015a). Advanced oxidation processes such as photo-Fenton oxidation process (Moncayo-Lasso et al. 2009), ultraviolet (UV) assisted sono-Fenton (Kakavandi et al. 2019), and ultrasonic irradiation assisted Fenton or Fenton like processes (Mahamuni and Adewuyi 2010) have been reported frequently in the literature.

Wastewater treatment using electrodialysis technique removes ionic pollutants as high voltage across ion exchange membrane is applied. When polluted water passes through the electrodialysis cell, anionic pollutants migrate toward the anode and the cationic one toward the cathode (Gunatilake 2015). The cation exchange membrane made up of poly vinyl chloride and 2-acrylamido-2-methylpropane sulfonic acid based hydrogel was prepared. The membrane had a low electrical resistance and showed high removal efficiency for $K^+$ (99.9%), $Pb^{2+}$ (99.9%), and $Ni^{2+}$ (96.9%) (Nemati et al. 2017).

## 11.3 Wastewater Treatment Through Adsorption Method

Adsorption is an efficient and cost-effective wastewater treatment method which involves retention of pollutants onto adsorbent's surface through forces such as electrostatic attraction, hydrophobic interaction, $\pi$–$\pi$ interactions, hydrogen bonding, precipitation, ion exchange, and surface complexation (Tan et al. 2015; Kumar et al. 2018; Patel et al. 2019). Adsorption can potentially be used to remove conventional as well as emerging pollutants from wastewater (Ali 2012; Patel et al. 2019). Adsorption process can remove inorganic and organic pollutants efficiently even up to 99% from water (Ali et al. 2012). Working efficiency of adsorption process depends upon concentration and type of pollutant, nature and particle size of adsorbent, structure, properties, and morphology of adsorbent like pore size, specific surface area, surface functional group, working *p*H, temperature, adsorbent dose, and contact time (Kumar et al. 2014; Patel et al. 2019). Adsorption process is preferred over the other conventional methods of wastewater treatment due to following reasons.

- Cheap adsorbents can be prepared from locally available agricultural residues and waste biomass.
- Selective adsorbents can be prepared by choosing appropriate biomass and their modification for intended application.
- Adsorption, unlike conventional wastewater treatments, generates no secondary pollutant or sludge.
- Adsorbent can be regenerated using physicochemical approaches.

### *11.3.1 Nanoadsorbents for Wastewater Treatment*

The commonly used conventional adsorbents for wastewater treatment are clay, lime stone, activated carbon, silica gel, activated alumina, and zeolite. These adsorbents have numerous challenges associated with them (i.e., expensiveness, rapid exhaustion, surface modification, and low removal efficiency). Adsorption efficiency of conventional adsorbents, like activated carbon, decreases rapidly in wastewater treatment process. Regeneration of these adsorbents requires thermal, chemical, oxidative treatments which increase the operational cost and thus limit adsorbent's application for pollutant removal (Crini 2005; Zhou and Lei 2006). Adsorption capacity of conventional adsorbents is affected by the presence of co-pollutants in wastewater (Makeswari and Santhi 2013). Moreover, relatively low removal capacities of conventional adsorbents limit their application in wastewater treatment. This is due to the poor morphological and structural properties. Thus, it is advisable to use smart, efficient, low-cost adsorbents in wastewater treatment process.

Nanoadsorbents which are cost-effective and efficient may be used in place of conventional adsorbents. Nanoadsorbents have large specific surface area, pore size, rich surface chemistry and density of active sites (El-Sayed 2020). Nanoadsorbents have widely been used for mitigation of conventional and emerging pollutants from (waste)water (Belessi et al. 2009; Joseph et al. 2019). A variety of nanomaterials, namely metallic nanoparticles, magnetic nanoparticles, nanostructured mixed oxides, carbonaceous nanomaterials (carbon nanosheets, carbon nanotubes, carbon nanoparticles), silicon nanomaterials (silicon nanotubes, silicon nanoparticles, and silicon nanosheets), nanoclays, nanofibers, xerogels, aerogels, and polymer-based nanomaterials have been used as adsorbents in wastewater remediation (Khajeh et al. 2013; El-Sayed 2020). Synthesis procedure and operating conditions influence the structural (specific surface area, particle size, pore size, and pore volume), chemical (functional group, acidic/basic character, surface potential, water solubility, stability) and thermal (conductivity, stability, heat capacity, volatile content) properties of nanomaterials. Different nanoadsorbents (graphene, $Fe_3O_4$, alumina, magnetite, carbon nanotube, $TiO_2$, $Al_2O_3$, mesoporous carbon, $MnFe_2O_4$, and nanozerovalent iron) have been synthesized by chemical vapor deposition, spray pyrolysis, thermal evaporation, vapor phase transport, electrodeposition, laser ablation processes, ion sputtering, coprecipitation using surfactants, chemical solution decomposition, and sol-gel method (Sharma et al. 2009; El-Sayed 2020). Sol-gel method is widely used for the synthesis of nanoparticles due to low cost, eco-friendliness, and homogenous product formation (Li et al. 2011).

Adsorption capacity of nanomaterials can be enhanced by modification such as composites formation and coating with other materials. For example, the composite of $TiO_2$ and carbon nanotubes has large surface area and active sites than the individuals, therefore having high removal capacity for pollutant removal (Ilisz et al. 2003; Hurt et al. 2006). Nanoparticles have been modified to increase the adsorption capability of the respective materials as the adsorption capacity is directly related to surface properties (Afkhami et al. 2010). Neat nanoparticles generally have a tendency to agglomerate in the absence of colloidal stability. So, the surface modification provides colloidal stability to nanoparticles (Crane and Scott 2012). Surface of nanomaterials can be modified through different mechanisms, namely ligand exchange, hydrothermal reduction, co-condensation, surface coating, covalent binding, grafting, and coprecipitation (Manyangadze et al. 2020). Modification of silica and iron nanoparticles has been sucessfully performed by hydrothermal method (Manyangadze et al. 2020). Nano size alumina, synthesized by chemical immobilization and modified with 2,4-dinitrophenylhydrazine was successfully removed $Cr^{3+}$ (97.4%), $Cd^{2+}$ (80.4%), and $Pb^{2+}$ (97.0%) from wastewater (Afkhami et al. 2010).

### 11.3.2 Agricultural Residue-Derived Nanoadsorbents for Wastewater Treatment

Agricultural residue-derived nanoadsorbents may remove pollutants efficiently from (waste)water. The use of agricultural residue-derived nanoadsorbents is a win-win strategy for wastewater treatment and its management simultaneously. The use of such nanoadsorbents will not only help in wastewater remediation but also serve as a smart remedy for agricultural wastes management which is otherwise a big challenge in itself. Herein, we have presented an overview of selected studies of agricultural residue-derived nanoadsorbents used for wastewater treatment. A summary of such nanoadsorbents has been provided in Tables 11.2 and 11.3.

**Table 11.2** Inorganic pollutants removal in water using agricultural residue-derived nanoadsorbents

| Agricultural waste | Materials | Surface area ($m^2/g$) | Contaminants | *p*H | Equilibrium time (min) | Adsorption capacity (mg/g) | References |
|---|---|---|---|---|---|---|---|
| Bagasse biomass | Carbon nanotube coated biochar | 359 | $Pb^{2+}$ | 4.0–5.0 | – | 122 | Inyang et al. (2015) |
| Corn straw | Nanocomposite (Zr@MCS) | 43.9 | $PO_4^{3-}$ | <7.0 | 60 | 29.2 | Hu et al. (2020) |
| Cotton wood | Biochar/AlOOH nanocomposite | – | $As^{5+}$ | – | 720 | 1.74 | Zhang and Gao (2013) |
| Cotton wood | Biochar/AlOOH nanocomposite | – | $PO_4^{3-}$ | – | 360 | 135 | Zhang and Gao (2013) |
| Pine wood | zerovalent iron/biochar nanocomposite | 13.6 | $As^{5+}$ | 4.0 | 60 | 124 | Wang et al. (2017) |
| Rice hull | Magnetic biochar/ZnS nanocomposites | – | $Pb^{2+}$ | 6.0 | 720 | 368 | Yan et al. (2015 b) |
| Rice husk | Nanoadsorbent | – | $Pb^{2+}$ | 8.0 | 70 | 3.78 | Kaur et al. (2020) |
| Sugarcane leaves (*Saccharum Officinarum*) | Nanoadsorbent | 75.4 | $Pb^{2+}$ | 7.0 | 30 | 148 | Kaliannan et al. (2019) |
|  |  |  | $Zn^{2+}$ | 7.0 | 30 | 137 |  |
| Walnut shell | β-cyclodextrin/chitosan | 82.0 | $Cr^{6+}$ | 2.0 | – | 206 | Huang et al. (2016) |
| Wheat straw | Nanocomposite Ws-N-La | 78.7 | $PO_4^{3-}$ | 3–7 | – | 30.0 | Qiu et al. (2017) |
| Wheat straw | Graphene/biochar nanocomposite | 17.3 | $Hg^{2+}$ | 7.0 | 72 × 60 | 0.85 | Tang et al. (2015) |

**Table 11.3** Organic pollutants removal in wastewater using agricultural residue-derived nanoadsorbents

| Agricultural waste | Materials | Surface area ($m^2/g$) | Contaminants | pH | Equilibrium time (Min) | Adsorption capacity (mg/g) | References |
|---|---|---|---|---|---|---|---|
| Artichoke leaves | Sodium hydroxide coated nanobiochar | 8.82 | Metformin hydrochloride (MFH) | 6.0–7.0 | – | 36.0 | Mahmoud et al. (2020) |
| Bagasse biomass | Carbon nanotube coated biochar | 359 | Sulfapyridine | 6.0–7.0 | 300 | 31.0 | Inyang et al. (2015) |
| Banana peel | Cellulose/$SiO_2$ nanocomposite | 8.92 | Methylene blue | 10.0 | 120 | 78.7 | Ali (2018) |
| Corn stalks | Magnetic $Fe_3O_4$ nanoparticles coated biochar | – | Crystal violet | 6.0 | – | 349 | Sun et al. (2015) |
| Cotton wood | Biochar/AlOOH nanocomposite | – | Methylene blue | – | 12 × 60 | 85.0 | Zhang and Gao (2013) |
| Cotton wood | Graphene coated biochar | – | Methylene blue | – | – | 174 | Zhang et al. (2012) |
| Dendro wood | Nanobiochar | 28.5 | Oxytetracycline | 9.0 | – | 113 | Ramanayaka et al. (2020) |
| Pine wood | Nanobiochar | 47.2 | Carbamazepine | 6.0 | 360 | 18.4 | Naghdi et al. (2019) |
| Rice straw | Nanocomposite of $SiO_2$-$Fe_3O_4$ | – | Penicillin G | 8.0 | 180 | 164.7 | Fakhrian and Baseri (2020) |
| | | | Amlodipine Besylate | 8.0 | 180 | 229 | |
| Sugar-beet pulp | Hydrogel nanocomposites (starch-based) | – | Crystal violet | 9.0 | 71 | 2500 | Moharrami and Motamedi (2020) |
| | | | Methylene blue | 9.0 | 146 | 1428 | |
| Wheat straw | Magnetic nanobiochar | 296 | Tetracycline | – | 12 × 60 | 263 | Li et al. (2020) |
| | | | $Hg^{2+}$ | | | 127 | |
| Wood pulp | Cellulose nanofiber | – | Congo red | – | – | 664 | Pei et al. (2013) |
| | | | Acid green 25 | – | – | 683 | |

#### 11.3.2.1 Silica-Based Nanoadsorbents

An amorphous silica based bionanoadsorbent (particle size: 10–50 nm, yield: 81%) was developed using rice husk via hydrothermal technique. The adsorbent successfully removed methylene blue (65% within a minute) from aqueous solution. Thermodynamic studies indicated the spontaneous and endothermic nature of adsorption process (Tolba et al. 2015). Rice husk residue-derived nanosilica ($SiO_2$) modified with polyelectrolyte polydiallyldimethylammonium chloride (PDADMAC) polymer was prepared by Pham and others. The modified $SiO_2$ with PDADMAC removed 92.3% amoxicillin antibiotic from aqueous medium. The mechanism involved was electrostatic attraction between cationic (PDADMAC polymer) and anionic surface ($SiO_2$). Non-electrostatic hydrophobic and lateral interactions were mainly responsible for amoxicillin (negatively charged) sorption onto modified nanosilica through induced electrostatic attractions (Pham et al. 2018).

Silica based bionanoadsorbents were prepared using barley and wheat grass with 92.4 and 93.0% of silica content, respectively. The barley and wheat grass based adsorbents successfully removed $Ni^{2+}$ (95% and 90% removal, respectively). The mechanism involved was electrostatic interaction between negatively charged surface of bionanoadsorbent and $Ni^{2+}$. Pseudo-first-order and Freundlich model described the adsorption kinetics and isotherm results, respectively (Akhayere et al. 2019). Further, a green bionanoadsorbent (99.6% pure nanosilica, 20 nm size) was prepared using rice husk and modified with polydiallyldimethylammonium chloride. The adsorbent removed beta-lactam cefixime efficiently (93.5% within 90 min) from aqueous solution. The electrostatic attraction between positively charged modified nanosilica and negatively charged cefixime was the major adsorption mechanism operated in removal process (Pham et al. 2020).

A thermally stable, efficient, eco-friendly, cost-effective, recyclable $Fe_2O_3$-enriched nanosilica ($SiO_2$-$Fe_2O_3$) was prepared from rice straw to remove Penicillin G (95%) and Amlodipine Besylate (65%) from aqueous solution. Langmuir adsorption isotherm and pseudo-first-order kinetic model indicated multilayer adsorption of pollutants on the heterogeneous adsorbent surface. The removal efficiency of $SiO_2$-$Fe_2O_3$ was 30% greater than pure $Fe_2O_3$ which indicates its effectiveness as an adsorbent for antibiotics removal (Fakhrian and Baseri 2020). Another cost-effective green bioadsorbent (silica nanoparticles) was synthesized using *Saccharum ravannae*, *Saccharum officinarum*, and *Oryza sativa* leaf biomasses through chemical method. Synthesized silica nanoparticles quantitatively removed $Pb^{2+}$ and $Cu^{2+}$ (>95%) from wastewater (Sachan et al. 2021).

#### 11.3.2.2 Cellulose-Based Nanoadsorbents

Cellulose nanofibrils were prepared using wood pulp treated with glycidyltrimethylammonium chloride via mechanical disintegration. The adsorbent efficiently retained congo red (0.95 mol/kg) and acid green (1.10 mol/kg) from wastewater (Pei et al. 2013). A green, recyclable cellulose-derived nanoadsorbent was prepared using sugarcane bagasse via bleaching treatment followed by acid hydrolysis. The developed adsorbent removed methylene blue efficiently (35 mg/g within 60 min) from wastewater. Langmuir and Freundlich adsorption isotherms indicated the possibility of both mono- and multilayer adsorption. The adsorbent could be used successively up to six cycles in both adsorption and desorption processes (Kardam et al. 2017). An efficient, carboxylcellulose nanofiber bioadsorbent was prepared using Australian spinifex grass via nitro-oxidation treatment. The adsorbent successfully removed $Cd^{2+}$ (84%) from aqueous solution. At low concentrations of $Cd^{2+}$ (<500 ppm), electrostatic interaction was prominent between the carboxylate groups of the adsorbent and $Cd^{2+}$, while at high $Cd^{2+}$ concentrations (>1000 ppm) dominant operating mechanism was precipitation followed by flocculation or coagulation (Sharma et al. 2018).

Banana peel-derived Cellulose/$SiO_2$ nanocomposite (particle size: 20 nm) was prepared using template-assistant method. Nanoadsorbent efficiently removed methylene blue (58.8 mg/g) from wastewater. The removal of pollutant followed Langmuir adsorption isotherm and pseudo-second-order kinetic model (Ali 2018). A starch-derived magnetic hydrogel nanocellulose crystal was prepared using sugar-beet pulp via acid hydrolysis method. The nanocomposites were used to remove methylene blue and crystal violet dyes from wastewater. Electrostatic force of attraction between anionic surface of modified nanocellulose and cationic dyes was main sorption mechanism (Moharrami and Motamedi 2020). Rice husk-derived magnetic carboxylcellulose nanofiber adsorbents (suspension, freeze-dried and nanocomposites) were prepared using TEMPO-oxidation method and used to remove $Pb^{2+}$ and $Ln^{3+}$ from wastewater. Among these, the adsorption capacity of nanocellulose suspension was maximum for $Pb^{2+}$ (193.2 mg/g) and $Ln^{3+}$ (100.7 mg/g). Electrostatic attraction between the negatively charged surface of adsorbent and metal ions was the main removal mechanism (Zhan et al. 2020).

#### 11.3.2.3 Lignin-Based Nanoadsorbents

An organosolv lignin nanobioadsorbent was prepared using steam-exploded rice straw biomass. The adsorbent removed methylene blue from wastewater (40.0 mg/g). The adsorption kinetics data were simulated by pseudo-first-order and pseudo-second-order models. Langmuir adsorption isotherm indicated the monolayer adsorption of methylene blue (Zhang et al. 2016 b). Lignin supported carbon nanotubes efficiently removed $Pb^{2+}$ (235 mg/g) and oil droplet (98.3%) from aqueous solution. Tridimensional structure, presence of ample oxygen functional groups, large specific surface area, water dispersibility, and mechanical stability of adsorbent made it an effective adsorbent for $Pb^{2+}$ removal. Pore diffusion and interaction between oxygen functional groups on the adsorbent surface and $Pb^{2+}$ were the responsible removal mechanisms (Li et al. 2017).

A cost-effective, recyclable, poly(ethyleneimine)-grafted-alkali lignin nanobioadsorbent fabricated with lanthanum hydroxide nanoparticles was prepared. The adsorbent successfully removed phosphate at high concentration (50 ppm, 94%, 60 min) and low concentration (2 ppm, 99 %, 15 min) under wide *p*H range (3.0-9.0). Surface precipitation and ligand exchange were the main operating mechanisms for adsorption (Zong et al. 2018).

Lignin-based nanoadsorbents (alkali lignin and lignin nanoparticles) were prepared and used successfully to remove Basic Red 2 (alkali lignin: 55.2 mg/g and lignin nanoparticle: 81.9 mg/g) from aqueous solution. The adsorbents were prepared via acidification of black liquor from paper factory waste. Alkali lignin was further modified by ethylene glycol treatment. Surface morphology and chemistry were confirmed by SEM and FTIR studies, respectively (Azimvand et al. 2018). An efficient, green, cost-effective, chitosan composite with nanolignin was developed and used to remove methylene blue (83%) from wastewater. The lignin was extracted from palm kernel shell using acid and tetrahydrofuran (Sohni et al. 2019). Pseudo-second-order kinetic model and Langmuir adsorption isotherm described the monolayer adsorption. Thermodynamic studies indicated the spontaneous endothermic adsorption of pollutant onto nanocomposite surface (Sohni et al. 2019).

Alkali lignin-based Pd nanoparticles were prepared via two different methods, namely loading followed by regeneration and regeneration followed by loading. The developed adsorbents removed toxic $Cr^{6+}$ by reducing it into less toxic $Cr^{3+}$. The adsorbent formed via regeneration followed by loading reduced $Cr^{6+}$ completely within 5 min (Chu et al. 2021). Lignin-based nano-trap multifunctional adsorbent was prepared via inverse-emulsion copolymerization method. The adsorbent removed soft metals ($Ag^{+}$, $Hg^{2+}$, $Cd^{2+}$) and borderline metals ($Pb^{2+}$, $Cu^{2+}$, $Zn^{2+}$) quantitatively (>99%) from aqueous solution to the level of permissible limit in drinking water. The silver-laden nanocomposite demonstrated antimicrobial activity towards *Escherichia coli* (99.68%) and *Staphylococcus aureus* (99.76%) (Xiao et al. 2019).

#### 11.3.2.4 Biochar-Based Nanoadsorbents

An engineered graphene-coated nanobiochar was prepared using cotton wood and used to remove methylene blue efficiently (174 mg/g) from aqueous solution. The synthesized nanobiochar was 20 times more efficient than unmodified biochar. The adsorption mechanism involved in removal process was strong $\pi$–$\pi$ interactions between fused aromatic rings of dye and the graphitic sheets of biochar (Zhang et al. 2012). A zinc modified novel nanobiochar was prepared using sugarcane bagasse and removed $Cr^{6+}$ from wastewater (~102 mg/g). The adsorbent worked even after sixth cycle of regeneration with a gradual decrease in performance (84.16–59.75 mg/g only). The working efficiency, regeneration capability, and economic feasibility made it an effective adsorbent (Gan et al. 2015). A nano zerovalent iron supported biochar was prepared using rice husk for industrial wastewater treatment through batch adsorption studies to remove methyl orange (98% within 10 min) (Han et al. 2015). Structural and physicochemical properties of biochar were confirmed by TEM, BET, and XRD techniques (Han et al. 2015).

A cost-effective, easily separable graphene modified nanobiochar composite was prepared using wheat straw. The adsorbent effectively removed phenanthrene and $Hg^{2+}$ from aqueous solution. Structure and morphology studies indicated the higher removal capacity of nanobiochar as compared to pristine biochar. The operating mechanism was π–π interactions. The larger surface area, greater thermal stability, and presence of ample functional groups on nanobiochar improved its adsorption capacity. Surface sorption and surface complexation were the pathways for Phenanthrene and $Hg^{2+}$ removal (Tang et al. 2015). A pine derived nano zerovalent iron modified biochar was prepared and the adsorbent used to remove $As^{5+}$ (124.5 g/kg within 1 h) from aqueous solution. The anoxic condition was more effective (about 8%) than the oxic conditions for removal of $As^{5+}$. Surface complexation and the reduction reactions were responsible removal mechanisms. Regeneration and high adsorption capacity of biochar makes it an effective adsorbent (Wang et al. 2017).

A pinewood derived nanobiochar (particle size: 60 nm) removed carbamazepine from aqueous solution (95% within 3 h) following pseudo-second-order kinetic and Freundlich adsorption isotherm model. The kinetic studies showed that the addition of surfactant enhanced the adsorption efficiency by 57% and increase in pH (from 3 to 8) improved the adsorption efficiency by 2.3-fold (Naghdi et al. 2019). A magnetic nanobiochar was prepared using wheat straw via ball milling. The adsorbent removed tetracycline and $Hg^{2+}$ from aqueous solution (>99%). The electrostatic interactions, hydrogen bonding, and π–π interaction between the surface of adsorbent and tetracycline were operating in case of tetracycline removal, while electrostatic attractions, Hg–π bond formation, and surface complexation were reported for $Hg^{2+}$ removal (Li et al. 2020).

### 11.3.3 Mechanism Involved in Adsorptive Removal of Inorganic and Organic Pollutants

Adsorption is a surface phenomenon wherein adsorbate molecules accumulate onto the surface of adsorbent. The presence of various minerals and functional groups remain present on the adsorbent surface. Various physical and chemical forces (mechanism) operate during sorptive removal of pollutants from wastewater using agricultural residue-derived nanoadsorbents. These forces allow the adsorption of different contaminants on adsorbent surface. Adsorption mechanism and efficiency are influenced by precursor materials of adsorbent and the characteristics of contaminants.

The physical properties of adsorbents such as surface area and pore volume and distribution play a vital role in adsorption of pollutants. Different mechanisms reported for sorptive removal of inorganic and organic pollutants from aqueous phase using agricultural residue-derived nanoadsorbents are depicted in Fig. 11.2a, b. The operative mechanisms in adsorption processes mainly included electrostatic

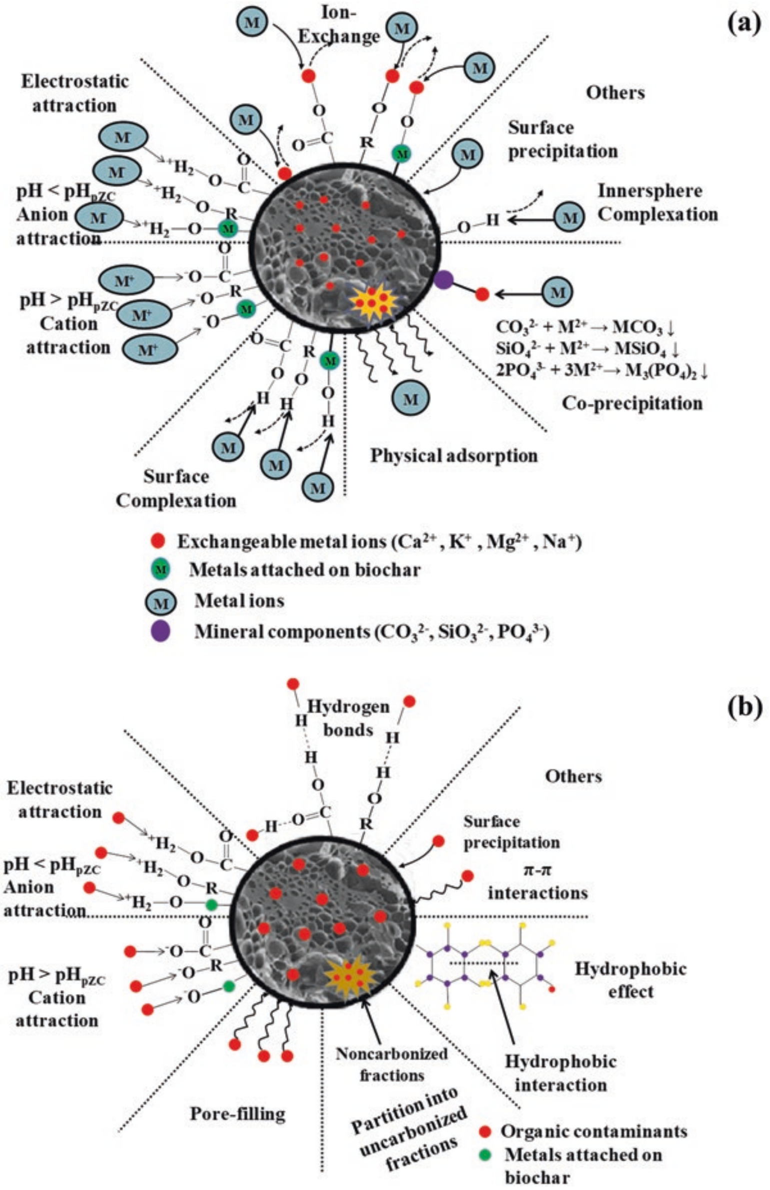

**Fig. 11.2** Mechanisms involved in sorptive removal of (**a**) inorganic and (**b**) organic pollutants. (Reproduced with permission from Tan et al. 2015)

attraction, hydrophobic interaction, π–π interactions, hydrogen bonding, precipitation, ion exchange, and surface complexation (Tan et al. 2015). Interaction between adsorbate and adsorbent also depends upon operational parameters like *p*H, matrix of the solution, contact time, pollutant concentration, adsorbent dose, temperature among the others.

If the solution *p*H is less than $pH_{pzc}$, then the functional groups present on the adsorbent surface will get protonated and adsorb negatively charged pollutant species from the solution; on the other hand if *p*H is more than $pH_{pzc}$ then positive charged species adsorb onto the surface. Wang et al. (2018) described various possible mechanisms between functionalized magnetic nanoparticles and metals, antibiotics, pesticides. In case of pesticides, mechanisms included hydrophobic interaction, electrostatic interaction, π–π interaction, π–π electron donor–acceptor interaction, π-stacking interaction, and physisorption. For antibiotic removal hydrogen bonding, π–π interaction, cation–π interaction, electrostatic attraction, electron-π donor–acceptor interaction, and amidation reactions were the possible mechanisms.

Coating on nanoparticles surface could improve the properties of adsorbents like increased active sites, large surface area, and improved removal efficiency. It has been observed that the coating of graphene on biochar attributed to the adsorption of organic pollutants through π–π interactions (Tang et al. 2015; Zhang et al. 2012). Both hydrophobic and π–π interaction may operate between the carbon nanotubes loaded bagasse biomass derived biochar and organic contaminant sulfapyridine (Inyang et al. 2015). Redox reaction and surface complexation were involved mechanisms for $As^{3+}$ adsorption onto cerium modified chitosan ultrafine nanobiosorbent (Zhang et al. 2016a). The monodentate and bidentate complexes formation mechanism involved between the hydroxyl groups of nanoadsorbent and $As^{3+}$ followed by oxidation of $As^{3+}$ to $As^{6+}$. Other mechanisms of adsorption like pore filling, partitioning, and electron donor-acceptor were also studied for the interaction of water contaminants with biochar-based materials. Zheng et al. (2013) found redox reaction between electron donor biochar and electron acceptor sulfamethoxazole. The functional groups like carboxylate and hydroxyl groups present onto the surface nanoadsorbents are responsible for interactions (ion exchange and electrostatic attraction) with inorganic contaminants like metal ions. Incorporation of nanosized material into adsorbent like biochar increases the surface active sites and surface area. For example, a nanocomposite biochar/AlOOH adsorbed arsenic and phosphate ions from the solution more effectively than pristine biochar (Zhang and Gao 2013).

### *11.3.4 Adsorbent Selection and Regeneration*

The selection of a treatment method involves economic, technical, and social considerations (Kumar et al. 2019). In terms of socio-economic aspect, an adsorbent should be cost-effective, readily available, developed from locally available materials, requires least technical expertise and should be easily applicable in large scale. For an adsorbent to be successful and sustainable in technical aspects include high sorption properties, high selectivity, high applicability in a wide range of contaminants concentration, easy applicability in vast ranges of matrices, and high reusability. Technical aspect of adsorbent selection can be evaluated through a variety of experimental assessment (Kumar et al. 2019; Patel et al. 2019; Ateia et al. 2020;

Mudhoo et al. 2021). For the better selection of an adsorbent, its physicochemical, morphological, and structural properties as well as contaminants removal capacity must be properly characterized (Patel et al. 2019). Both batch and dynamic sorption studies must be conducted followed by adsorbent regeneration studies. Batch sorption studies help in the optimization of adsorbent properties during its developmental stage (Choudhary et al. 2020; Patel et al. 2021), while dynamic studies simulate the real-world scenarios of the adsorbent applicability. Thus, agricultural residue-derived nanoadsorbent with minimum chemical utilization, low cost, easy preparation and wide applicability would be the adsorbent of choice.

Regeneration of nanoadsorbents leads to the applications such as reusability of nanoadsorbent and recovery of valuable metal species. Regeneration of exhausted adsorbent is essential to revive its adsorption capacity. It involved the stripping off the adsorbed metals or other contaminants so that the adsorbent can be used again and again. Due to this stripped metals can be recycled back to the process of origin, it makes the adsorption method economically viable. In the several regeneration cycles, the adsorption capacity decreased to some extent due to decrease in surface area and active sites. For the recovery of metal ions mainly dilute acids ($HNO_3$, $H_2SO_4$, and HCl) are used. Hu et al. (2020) synthesized a cheap adsorbent (Zr@MCS) for phosphate removal by incorporation of nanosized $Zr^{4+}$ oxide onto amino modified corn straw. Zr@MCS successfully adsorbed the phosphate ions and this loaded Zr@MCS regenerated using 5% NaOH–NaCl solution. After the first regeneration it was found that the removal efficiency decreased from 70% to 65% and after 2–8 runs the efficiency decreased only up to 63%. Further, phosphate was regenerated from phosphate-rich desorption solution by struvite crystallization method and used as phosphate fertilizer in soil. 0.5 M NaOH solution was used for $Cr^{6+}$ desorption from β-cyclodextrin–chitosan modified biochar by Huang et al. (2016) and it was analyzed that after the five adsorption-desorption cycles the removal capacity decreased up to 56%. Nanobiochar from artichoke leaves was synthesized and modified with NaOH to adsorb antidiabetic drug Metformin hydrochloride (MFH) from the solution (Mahmoud et al. 2020). MFH loaded Artich-Bch-NaOH then regenerated using 0.1 M HCl. For this, first of all Artich-Bch-NaOH-bounded-MFH dried at 70 °C and treated with 0.1 M HCl for 40–45 min, filtered and dried at 70 °C. The regenerated adsorbent was then used about 4–5 times and it was estimated that even after 5 cycles the adsorption capability was in the range 78.5–82.0%. So, for the economic reasons it should be ensured that prepared adsorbent can be used several times.

## 11.4 Conclusion and Recommendations

Adsorption is an easy to use and economic wastewater treatment unit process. However, the design and development of an effective, cheap and specific adsorbent is a challenge. The conventional adsorbents (for example, clay, lime stone, silica, soil, zeolite, activated charcoal, activated alumina) have certain challenges associated with them like high cost, difficulty in surface modification, regeneration, exhaustion, and low pollutants removal efficiency. Nanoadsorbents prepared using low-cost and abundantly available agricultural residue may help to deal with the above said constraints associated with the conventional adsorbents. Agricultural residue-based nanoadsorbents (silica, cellulose, lignin, biochar) might be ideal candidates being cost-effective, eco-friendly and effective for conventional emerging pollutants removal from (waste)water. These adsorbents must be made more smart through surface functionalization, composite formation and improving their reusability for emerging pollutants removal in aqueous phase. Future studies must focus on exploring mechanistic aspects of wastewater remediation using novel agri-residue-based nanoadsorbent. Agricultural residue-derived nanoadsorbents are expected to have a great future in the wastewater purification sector.

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# Chapter 12
# State-of-the-Art and Perspectives of Agro-Waste-Derived Green Nanomaterials for Wastewater Remediation

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**Abstract** Substantial urbanization and industrialization practices lead to increased wastewater production, ultimately causing environmental pollution and chronic diseases in living beings. Conventional technologies used for wastewater remediation are quite expensive, cumbersome, and less efficient. Owing to the world's basic need for clean and pure water, in the past decade, research interests are being focused on exploring new technologies and materials for water purification, which has been given rise to the use of agro-waste-derived green nanomaterials as an economically viable and sustainable alternative for this purpose. Agro-wastes are increasing day by day and their dumping in landfills or water bodies is posing a serious threat to our mankind and ecosystem. This chapter aims to present a broad overview of the recent use of agro-wastes to generate green nanomaterials which have been utilized in wastewater remediation. Herein, we will highlight certain advantages of such nanomaterials like low cost, reusability, consumption of fewer chemicals during synthesis, high adsorption, and removal efficiency in the elimination of toxic heavy metals, dyes, bacteria, organic and inorganic pollutants, halogens, etc. from wastewater. In the next section, a detailed description of different agro-wastes used for green nanomaterials production will be given along with their sources, properties, and utilization of such nanomaterials in wastewater remediation. Then, future perspectives of this work followed by conclusions and recommendations will be explained. In the present scenario of circular economic development, management of agro-wastes in an appropriate manner, formation of green nanomaterials from these agro-wastes, and their application in wastewater

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treatment not only mitigate the problem of environmental pollution but also uplift socio-economic level by creating new job avenues.

**Keywords** Agro-wastes · Green nanomaterials · Wastewater remediation · Conventional technologies · Environmental applications

## 12.1 Introduction

Water is considered as the "essence of life," essential for the sustainment of living beings. Around 70% part of the Earth is covered with water in form of oceans, rivers, lakes, glaciers, snow, etc., yet more than one billion human population still do not have access to clean drinking water resources (Kurniawan et al. 2012) and within 25 years, about one-third of the total potable water resources will be depleted. In Asian and African countries, most of the population is suffering from the problem of scarcity of pure drinking water. Blasting increase in population rate, industrialization, and urbanization are not only enhancing the water scarcity issue but also polluting natural water resources, and ultimately create economic and environmental challenges. Various human activities cause water pollution by discharging heavy metals, dyes, fertilizers, oil, detergents, chemicals, grease, phenolic compounds, polycyclic aromatic hydrocarbons, etc. in aquifers. These organic and inorganic contaminants are highly toxic, carcinogenic, perilous, and can cause severe damages to the lungs, kidneys, heart, central nervous system, and other vital organs even at ppm concentrations. More than 200 million people die every year worldwide due to waterborne diseases (Amin et al. 2014) which have drawn the attention of scientists and governments towards wastewater remediation or treatment. Since ancient times we have been practicing traditional methods for water purification like filtration, sedimentation, coagulation, disinfection, etc., but their massive use requires more time, cost, infrastructure, manpower, etc. This paved a way for the development of new methodologies for water treatment, including adsorption, electrolysis, reverse osmosis, membrane filtration, flocculation, photocatalytic oxidation, nanofiltration, etc. (Lee et al. 2014; De Gisi et al. 2016; Tran et al. 2017; Hube et al. 2020; Lin et al. 2020; Rashid et al. 2021). Among these prevailing technologies, method of adsorption has been proved to be more beneficial, cost-effective, potential, and eco-friendly for wastewater remediation (Qasem et al. 2021). Some classical adsorbents such as zeolites, clay, silica gel, activated carbon, biochar, etc. have been reportedly used several times for efficient removal of different contaminants from wastewater (Çeçen and Aktaş 2011; Shi et al. 2017; Manyuchi et al. 2018; Bilgiç and Çimen 2019; Samara et al. 2019). Nevertheless, these adsorbents cannot remove oil and certain heavy metals up to a higher extent (Tripathi and Rawat Ranjan 2015; Anjum et al. 2019), so, it is crucial to explore new, more promising adsorbents. In this sequence, the use of nanotechnology and nanomaterials was found to be superior in the case of environmental remediation, particularly, wastewater treatment (Farghali et al. 2013; Jun et al. 2018; Taher et al. 2018).

Nanomaterials are materials having particle sizes with at least one dimension less than 100 nm. Owing to their larger surface area, lesser particle size, and other remarkable physical, chemical, mechanical, optical, magnetic, electrical, and thermal properties, nanomaterials have been playing a significant role as adsorbents in removing most of the water pollutants as compared to macro sized materials. Nanotechnology and nanomaterials are expedient in the fast detection and elimination of water contaminants and provide a more accurate, low-cost solution to the problem of wastewater treatment. Generally, nanomaterials such as metal oxides, metal carbides, layered double hydroxides, magnetic nanomaterials, polymer nanocomposites, gels, carbon-based nanomaterials (carbon nanotubes, graphene, fullerenes, activated carbon), etc. are used for adsorption of water pollutants (Mohmood et al. 2013; Yang et al. 2019; Gusain et al. 2020). However, such nanomaterials are quite expensive which confined their bulk scale use on a commercial scale. Thus, there is a burning requirement to develop cost-efficient, environmentally benign materials as sustainable alternatives in green nanomaterials production.

Green nanomaterials are usually synthesized by natural, eco-friendly precursors like plant extracts, biopolymers, bio-organisms like algae, fungi, waste materials, etc. (Das et al. 2020; Nasrollahzadeh et al. 2020). Agro-wastes like rice husk ash, wheat husk ash, corn cob, sugarcane bagasse, etc. could be potential candidates for the synthesis of green nanomaterials. Many carbon-based nanomaterials, metal/metal oxide-based nanomaterials have been produced by utilizing these agro-waste materials and exploited in various fields, namely, catalysis, adsorption, environmental remediation, photocatalysis, etc. (Qiu et al. 2019; Rao and Rathod 2019; Teimouri et al. 2019). The chief advantages of using agro-wastes in preparing green nanomaterials for wastewater remediation are: (1) low cost, (2) eco-friendly, (3) easy to regenerate and reuse, (4) high efficiency, (5) alternative solution to generate value-added materials from waste materials, and (6) helps in solid waste management. Presence of porous structure, various functional groups like –OH, –COOH, etc. in agro-wastes enhances their sorption capacity. This chapter provides an insight into various conventional as well as prevailing technologies used for wastewater remediation. A brief overview of the synthesis, properties, and advantages of nanomaterials has been given. Characterization techniques that help in analyzing nanomaterials are also explained. Then, a review about various agro-wastes which have been utilized for the generation of green nanomaterials has been given along with their potential applications in wastewater remediation. In the end, prospects, recommendations, and challenges associated with this application are elucidated. This chapter outlines that the synthesis of green nanomaterials from agro-waste materials and applications in wastewater remediation presents a good opportunity in research in nanotechnology, formation of safe nanomaterials at a larger scale, and simultaneously imparts a fair solution to the problem of proper management and disposal of such waste materials which are usually discarded in water bodies and landfills.

## 12.2 Conventional Technologies Used for Wastewater Remediation

The introduction of various inorganic and organic pollutants into water bodies is an alarming situation for the environment. These pollutants get entered into the water system via different industrial activities such as textile industries, mining, paper industries, electronic industries, agricultural industries, tanneries, etc. (Alalwan et al. 2018), which cause serious health issues in human beings as well as adversely affect aquatic animals and plants. Numerous conventional methods for the removal of these pollutants from water bodies are reported in the literature. Some of the commonly used conventional methods are chemical precipitation, ion exchange, chemical oxidation/reduction, reverse osmosis, electrodialysis, and ultrafiltration (Taka et al. 2017; Acharya et al. 2018). A summary of these methods along with their advantages and disadvantages is given in Table 12.1.

## 12.3 Nanomaterials for Wastewater Remediation and Their Advantages

Materials whose one of the external dimensions is in the nanoscale, i.e., between 1 and 100 nm are nanomaterials. Sometimes such materials also have an internal surface or structure in the nano range. Nanomaterials owing to their specific structure-dependent, remarkable physicochemical, thermal, mechanical, optical, electrical, and thermal properties have been playing a considerable part in revolutionizing the industrial growth of this world. Figure 12.1a shows different types of nanomaterials reported so far. Nanomaterials can also be classified based on the number of dimensions—zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) nanomaterials, as shown in Fig. 12.1b. Nanomaterials in which all three dimensions are in the nano range are zero-dimensional nanomaterials. In one-dimensional nanomaterials, two dimensions are in the nano range, while in two-dimensional nanomaterials, one dimension is at the nanoscale. Three-dimensional nanomaterials themselves do not have any dimension in the nano range but they are composed of nanosized particles and crystals arranged in different orientations, layers to form nano interface or surface. Nanomaterials can be synthesized by using chemical and physical methods as summarized in Fig. 12.1c while nanomaterials prepared by using biogenic methods, waste precursors, eco-friendly, safe, natural materials are green nanomaterials.

Various characterization techniques are used to analyze the size, shape, properties, surface area, etc. of nanomaterials. Surficial properties like shape, size, charge, and surface area of nanomaterials are detected by scanning electron microscopy, transmission electron microscopy, field emission scanning electron microscopy, environmental scanning electron microscopy, atomic force microscopy, zeta potential, Brunauer–Emmett–Teller physisorption methods. Structural properties are

**Table 12.1** Conventional methods for water treatment

| Name of the method | Details of the method | Advantages | Disadvantages |
|---|---|---|---|
| Chemical precipitation | This method involves the precipitation of heavy metal ions via a reaction between a chemical agent and heavy metals. Thus-produced precipitate is separated from water by sedimentation or simple filtration process. This method includes hydroxide precipitation and sulfide precipitation. | Easy, less expensive, can remove almost all the metals. | A huge amount of sludge is formed during this process. |
| Chemical coagulation | Chemical coagulation is a process in which colloidal particles are destabilized via a charge neutralization process. The most common coagulants used for this process are $Al_2(SO_4)_3$, $FeSO_4$, $FeCl_3$, etc. | Low cost, easy operating conditions, having wide pH range, high capacity, fast kinetics, effective on a wide range of pollutants. | Excessive use of chemicals, formation of sludge, dewatering is required. |
| Wet oxidation | This process is carried out in the presence of some oxidizing agents like air, $Cl_2$, $O_3$, etc. or oxygen. | Require fewer chemicals, consume less energy, easy to operate. | $Cl_2$ gas is toxic and produces hazardous by-products, $O_3$ gas requires high electricity, which increases the cost of the process. In addition, it produces hazardous by-products, and this process requires high temperature and pressure conditions. |
| Electrochemical oxidation | This method involves the passage of an electric current in wastewater, due to which a redox reaction occurs. This results in the deposition of metal ions on the cathode and pure metal can recover. The most common electrochemical oxidation methods are: electrocoagulation, electroflotation, and electrochemical precipitation. | The process is metal-specific, fewer chemicals are required, recovery of pure metal can be attained. | Expensive process due to significant energy input, regular replacement of the electrodes is needed, an inefficient process for highly polluted water. |

(continued)

**Table 12.1** (continued)

| Name of the method | Details of the method | Advantages | Disadvantages |
|---|---|---|---|
| Photocatalysis | In this process, organic pollutants get oxidized by photocatalysts into non-toxic products like water, $CO_2$ and can also disinfect certain bacteria.<br>Photocatalysts generate hydroxyl free radicals by generating electron-hole pairs. This –OH free radical then initiates secondary reactions. | Removal of metals and organic pollutants takes place simultaneously, formation of less harmful by-products. | High energy input is required, the clarity of the water is important for penetration of UV light, the cleaning of the light source (UV lamp) increases the cost of the process, the process is not efficient for hard water. |
| Ion exchange | This method involves the exchange of ions between ion exchange resin and polluted water. Ion exchange resins are made up of organic or inorganic polymeric materials. | The ion exchange resin can easily be regenerated, reused, the process is metal-specific, the removal process is fast. | An expensive process, less metal ion removal capacity. |
| Reverse osmosis | In this method, a semi-permeable membrane is used to separate impurities from the water. This membrane allows water to pass through it at high pressure and refuse the contaminants. | Less solid waste produced, high efficiency (>95% for single metal), small space requirement. | High pressure requires significant energy input, large amount of chemicals is required for washing of membrane, quite expensive process. |
| Adsorption | This method is a widely utilized method for the treatment of wastewater. Various conventional adsorbents such as activated carbon, ion exchange resins, and others are used for this purpose. In most of the processes, the pollutant molecules are adsorbed in the pore structure of carbonaceous materials. | Low cost, easy operating conditions, having wide pH range, high capacity, fast kinetics, a wide variety of target pollutants. | Low surface area, less active sites on the adsorbent surface. The selectivity and specificity of the process are less. |

(continued)

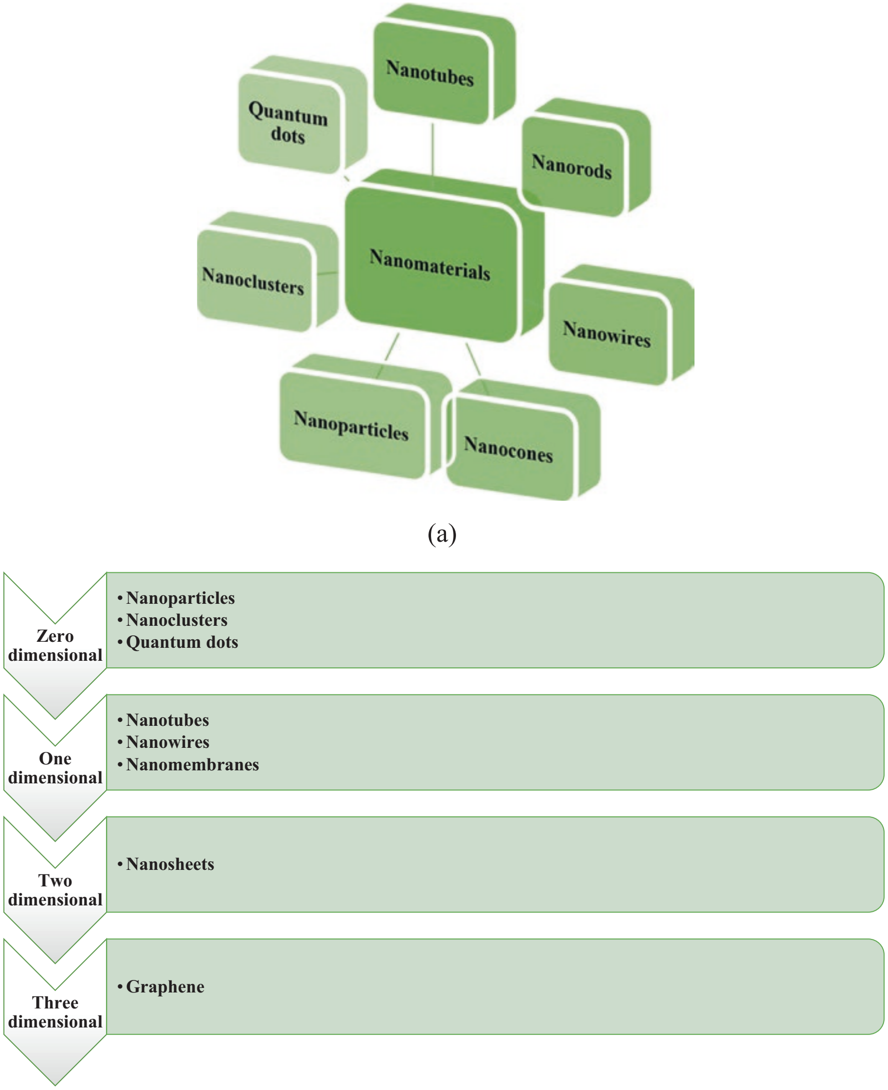
**Table 12.1** (continued)

| Name of the method | Details of the method | Advantages | Disadvantages |
|---|---|---|---|
| Biological treatment | This method is mainly applicable to the removal of organic pollutants and inorganic non-metals from wastewater. | Cost-effective, effective removal of pollutants from waster, environmental benign process. | Process efficacy is dependent on the activity of the microorganisms, seasonal changes also affect the efficacy of the process, high maintenance of biofilters and bioreactors are required. |
| Ultra-filtration | In this method, a permeable membrane is used to separate heavy metals from other impurities according to their pore size and molecular weight. | Less amount of by-products is produced, requires less space, is easy to operate, requires fewer chemicals, removes a high amount of impurities, requires low pressure. | Expensive, requires high maintenance of membrane, removal (%) decreases with the presence of other metals, complicated process. |
| | For a higher metal recovery, two types of filtrations, namely micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) can be used. | | |

studied by X-ray diffraction, X-ray photoelectron spectroscopy, and nuclear magnetic resonance spectroscopy. Thermal properties are analyzed by thermogravimetric analysis and differential scanning calorimetry, and magnetic properties are determined by magnetic force microscopy and vibrating sample magnetometer. The bonding of nanomaterials is determined by Fourier transform infrared spectrometry, Raman scattering spectroscopy, and ultraviolet-visible spectroscopy. The chemical composition of nanomaterials is determined by energy-dispersive X-ray spectroscopy and X-ray fluorescence.

### *12.3.1 Some Advantages of Nanomaterials in Wastewater Remediation*

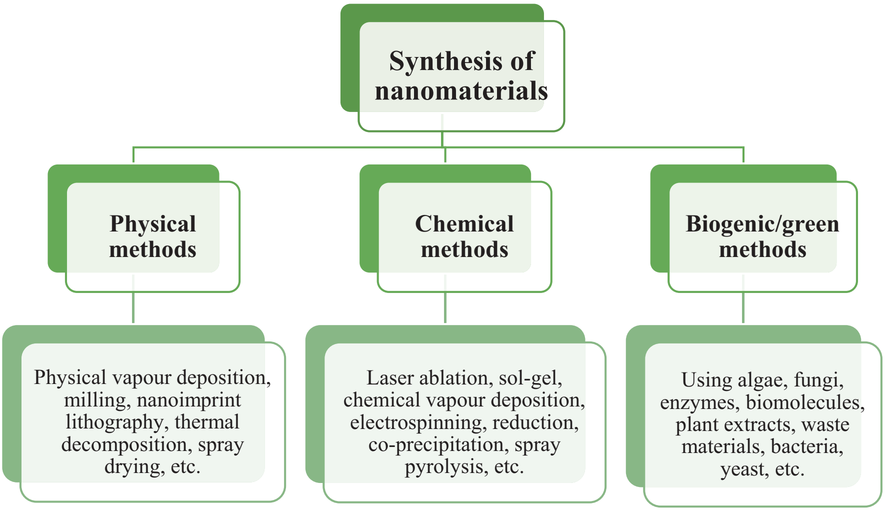
Strong adsorption capacity, small size, larger surface area, high reactivity, conveniently regenerable, metal/metal oxides based nanomaterials are antibacterial, disinfectant, antimicrobial, cost-effective, thermally stable, pH tolerant, and magnetic nanomaterials are easily recoverable through filtration in presence of external magnetic field. Fast kinetics, biodegradable, environment-friendly, biocompatible, high stability, long shelf life, good mechanical strength, porosity, better dispersion,



(b)

**Fig. 12.1** (**a**) Different types of nanomaterials reported so far, (**b**) classification of nanomaterials, and (**c**) common methods used for the synthesis of nanomaterials

enhanced catalytic activity, easily accessible, quantum-size effects that increase energy bandgap and shrink particle size, good selectivity, high treatment efficiency, reduction in time and labor are other important aspects involved in utilization of nanomaterials in wastewater remediation.



(c)

**Fig. 12.1** (continued)

## 12.4 Agro-Waste-Derived Green Nanomaterials for Wastewater Remediation

To overcome the limitations of the aforementioned conventional wastewater remediation techniques, some eco-benign, economic methods have been developed recently, using green nanomaterials. Agro-waste-derived green nanomaterials generally undergo adsorption process for the safe and fast removal of pollutants from wastewater. In the recent scenario, researchers are showing their interest in the use of agro-waste materials as green nano adsorbents due to their chemical composition, unique physiochemical properties, low cost, and easy availability (Isikgor and Becer 2015; Ferronato and Torretta 2019; Saravanan et al. 2021). Agro-waste materials are basically lignocellulosic materials. Their adsorption capacity mainly depends upon their chemical composition, surface morphology, physicochemical properties, and surface active sites (Gupta 2015; Bital et al. 2018).

Agro-waste material based nano adsorbents can be synthesized via simple mechanical and physical activation techniques in which crushing and milling are involved (Jeyaseelan and Gupta 2016). Due to this their particle size gets reduced thus increasing the surface area. For example, waste leaves and peels can be converted into efficient adsorbents via simple grinding. This resulted into a powder of higher surface area (Ponnuchamy et al. 2020). Some other advanced techniques can also be employed to obtain an efficient adsorbent with increased adsorption capacities (Reza et al. 2020). In the following section, some agro-wastes based nano adsorbent materials like carbon-based nanomaterials, metal, and metal oxides, etc.

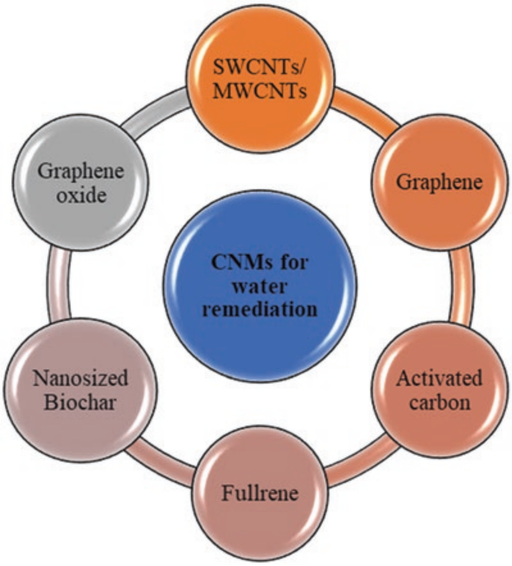


**Fig. 12.2** Carbon-based nanomaterials used for water remediation

have been discussed which are being used to remove inorganic and organic pollutants from the wastewater in the past decade.

### 12.4.1 *Carbon-Based Nanomaterials for Water Remediation*

Recent studies explored the utilization of environmentally friendly carbon-based nanomaterials for wastewater treatment. The most common carbon-based nanomaterials are carbon nanotubes (CNTs): single-walled carbon nanotubes (SWCNTs)/multi-walled carbon nanotubes (MWCNTs), graphene, graphene oxide (GO), nanosized biochar, activated carbon, and fullerene, as shown in Fig. 12.2 (Cha et al. 2013). These carbonaceous nanomaterials are categorized based on their geometrical structure like graphene and graphene oxide is a 2D allotropic form of carbon, SWCNTs and MWCNTs are tube-shaped, and fullerenes are spherical.

#### 12.4.1.1 Activated Carbon

Activated carbon (AC) consists of aromatic carbon atoms arranged in a disorganized form. It is a versatile adsorbent with a high surface area (500–2000 $m^2/g$), tuneable pore structure, chemical and thermal stability (Foo and Hameed 2010; Chen et al. 2011b). The adsorption done on the microcrystalline surface of AC is accompanied by functional groups (Gross and Nowak 2010). AC adsorbents are widely used in the removal of heavy metals contaminants (Bital et al. 2013). The conventional synthesis of AC involves various precursors like coal, wood, petroleum, polymers, etc., which are costly, non-renewable, and available in a limited amount. To overcome this, several renewable resources such as agro-wastes and biomaterials are employed as a precursor to synthesize nanosized activated carbon for water remediation (Keng et al. 2014).

Agro-wastes with high carbon content are the best precursors to synthesize AC (Gupta 2015; Díaz-Muñoz et al. 2016). Lignin and cellulose present in these wastes have high adsorption capacity and can adsorb different metal ions from the wastewater (Saravanan et al. 2015). The physicochemical properties of agro-waste-derived AC can be easily modified (Vivo-Vilches et al. 2014). AC can be synthesized using agro-wastes as precursors via different activation techniques such as physical, chemical, physiochemical, microwave, etc. as given in Fig. 12.3. Physical activation is a two-step process consisting of carbonization followed by oxidation, while chemical activation is a single-step process using some chemical agents like NaOH, KOH, $H_3PO_4$, etc. Physiochemical activation consists of use of heat and chemicals and microwave method involves use of microwave radiations in synthesis of AC from agro-wastes (Reza et al. 2020).

The mechanism of adsorption with AC involves dissociation of functional groups present on the surface of AC, which attracts opposite charged ions from the contaminated aqueous solution thus produced electric charges (González-García 2018). Recently, several green nanoparticles loaded AC such as $WO_3$/AC, FeO/AC, and Ag/AC for removing pollutants from the wastewater have been acknowledged by various researchers (Sahu and Behera 2017; Anfar et al. 2018). The removal efficiency of AC nanocomposites depends upon the pH of the solution. Acidic solutions attract anions while alkaline solutions attract cations, thus acidic adsorbents retain cations while basic adsorbents retain anions (Rivera-Utrilla et al. 2013).

Heavy metal pollutants like Cd, Pb(II), Cu, Fe, and Cr(VI) present in water can be removed using AC (Yusuff 2019). The removal efficiency is affected by metal ion-AC interaction, pH of the solution, surface morphology of the AC, types of

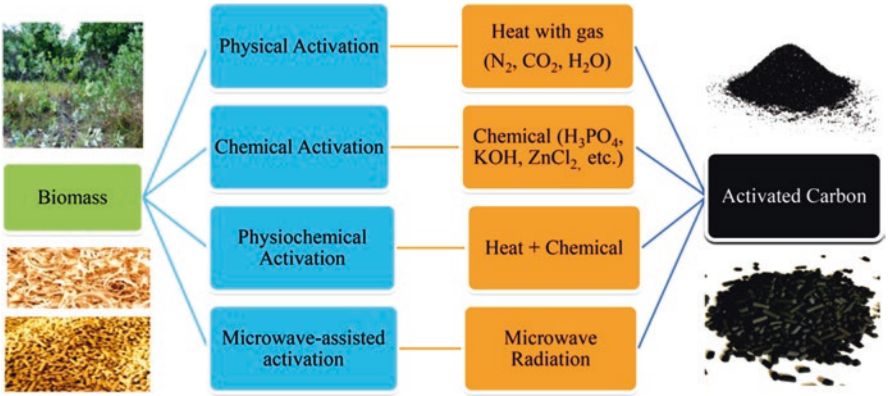


**Fig. 12.3** Synthesis of AC via different activation techniques (Reza et al. 2020)

functional groups, size of metal ions, etc. (Bian et al. 2018). A group of researchers has synthesized Tamarind wood-derived AC via chemical activation and applied it in wastewater treatment (González-García 2018). In a similar study, date pits derived AC was also found efficient to remove Cd at 6 pH and approximately 30 °C temperature (Ahmed 2016a, b). The removal of mercury from polluted water has also been performed over chemically activated pistachio wood waste-derived AC and the results showed that the adsorption was done at a high adsorption capacity of about 200 mg/g (Sajjadi et al. 2018). Some studies compared the adsorption capacities of AC prepared via physical and chemical activation and it was found that the removal of Cr(VI) over chemically activated AC was much more than the physically activated AC. In this context, physically activated iron-loaded walnut shell derived AC showed low adsorption capacity (30 mg/g) (Derdour et al. 2018), while chemically activated chestnut oak shell derived AC showed high adsorption capacity (85.47 mg/g) towards Cr(VI) removal (Niazi et al. 2018).

Agro-waste-derived AC is also found effective for the removal of dyes from wastewater. A study showed the removal of methylene blue dye over rice straw derived AC with high adsorption capacity of 129.5 mg/g (Ahmed 2016a, b). Physically and chemically activated date pits derived AC has been employed for the removal of several dyes such as methylene blue, methyl orange, and many others but the best adsorption capacity was observed with $ZnCl_2$ and KOH activated AC for removal of methyl orange and methylene blue, respectively (Ahmed 2016a, b). Malachite green dye was also removed effectively using *B. Aethiopum* flower and rambutan peels derived chemically activated AC with 48.23 mg/g and 418.6 mg/g adsorption capacities, respectively (González-García 2018).

In another study, Anfar et al. (2018) investigated the adsorption behavior of coconut husk and almond shell derived AC loaded with $WO_3$ nanoparticles towards the removal of methylene blue and Rhodamine B dye. The adsorption results indicated that $WO_3$/AC showed high adsorption capacity (1666.67 mg/g) for Rhodamine B. The high adsorption capacity of $WO_3$/AC may be due to the loading of nanoparticles which may affect the removal efficiency (Anfar et al. 2018).

The removal of phenolic compounds from polluted water has also been reported on agro-waste-derived AC. The phenolic compounds can be removed via a donor-acceptor mechanism where the hydroxyl groups of AC react with the aromatic ring of phenolic compounds (Mu'azu et al. 2017). A recent study showed the removal of Bisphenol A by using argan nutshell derived AC with high adsorption capacity (1250 mg/g) (Zbair et al. 2018). Another investigation reported the use of apricot stone derived AC for removing aniline. The results showed that $ZnCl_2$ activated AC was a much efficient adsorbent as compared to $H_3PO_4$ activated AC (Kecira et al. 2018).

Other investigations include the removal of toluene, *p*-nitrotoluene, benzene, and formaldehyde over durian shell AC, orange peel AC, coconut shell AC, and coffee residues AC, respectively. The maximum adsorption efficiency (874 mg/g) was obtained with Durian shell AC for removal of toluene (González-García 2018).

#### 12.4.1.2 Biochar

Biochar (BC) is a carbonaceous material produced from agro-wastes and other lignocellulosic materials. It has potential applications in removing pollutants from wastewater and increasing the fertility of the soil (Shaheen et al. 2018; Bandara et al. 2019; Quan et al. 2019; Palansooriya et al. 2019). BC is a highly porous material containing different functional groups such as –COOH, –OH, and phenolic –OH. The porosity and presence of these functional groups make it an appropriate adsorptive material for the removal of various organic and inorganic pollutants from wastewater. In general, the particle size of biochar ranges from micrometers to centimeters, which is accountable for its better adsorption capacity (Taheran et al. 2016). Recently researchers have focused their attention to reduce the particle size in the nano range (100 nm or below) so that the surface area of BC can increase, which can further increase its adsorption potential (Chen et al. 2017).

The conventional biochar has limited adsorption capacity and also it is not easily separable from the adsorption medium (Reddy and Lee 2014). In contrast, nanobiochar has great adsorption potential due to its improved physiochemical properties. A study has demonstrated the high adsorption capacity of nanobiochar due to its high surface area and enhanced physiochemical and thermal properties. Additionally, the number of functional groups in nanobiochar is also increased which increases the interaction between BC and the pollutants (Ramanayaka et al. 2020).

Of late, BC is effectively utilized for the removal of pesticides from wastewater (Oliveira et al. 2017; Ameta and Ameta 2018). Recently, Naghdi et al. have synthesized nanobiochar using pine wood as a precursor via mechanical activation. The particle size of synthesized nanobiochar was 60 nm. The high adsorption capacities of thus obtained nanobiochar were obtained in the removal of carbamazepine from polluted water (Naghdi et al. 2017). Furthermore, activated biochar prepared from calligonum comosum having a high specific surface area of 1473 $m^2/g$ and oxygen-containing functional groups were investigated to adsorb atrazine from water. The results indicated that the highest adsorption (714.3 mg/g) of atrazine was observed at neutral pH and 40 °C temperature of the solution (Alahabadi and Moussavi 2017).

Several heavy metal ions such as As, Pb, Cr, and Cu are reported to be removed from the polluted water by using nanobiochar as adsorbents. A group of researchers has studied the adsorption of tetracycline and Hg(II) from polluted water with the help of mechanically activated magnetic nanobiochar. The results suggested that the nanobiochar showed high adsorption capacity with 99% removal of both the pollutants (Li et al. 2020a, b). Another study investigated the bioremediation of phosphate ions, chemical oxygen demand (COD), and ammonium ions from wastewater. For this, a biologically active iron-loaded nanobiochar absorbent was successfully employed with a removal efficiency of almost 90%. The use of different chemically activated nanobiochar in adsorption is also reported in the literature. For example, $KMNO_4$ treated biochar, NaOH treated biochar, and $FeCl_3$ treated biochar are reported to remove Cd(II) from polluted water. $KMNO_4$ treated biochar has shown the maximum adsorption capacity (81.1 mg/g) with a high adsorption rate (14.46 g/(mg h)) (Li et al. 2017). In a similar study, $Fe_2O_3$ loaded nanobiochar derived from rice husk was employed in the removal of As with more than 90% adsorption capacity (Nath et al. 2019). Some agro-waste-derived nanobiochar and biochar nanocomposites used for removal of pollutants from wastewater are summarized in Table 12.2.

**Table 12.2** Pollutants removal by biochar nanocomposites and nanobiochar

| Precursor | Adsorbent | Pollutants | Results | Reference |
|---|---|---|---|---|
| Cottonwood | MgAl-layered double hydroxide-biochar | Phosphate ions | 410 mg/g | Zhang et al. (2013) |
| Rice husk | RH300, RH500, RH700 | Pb(II) | RH500 and RH700 showed maximum adsorption | Shi et al. (2019) |
| Wheat straw | Ball milled magnetic biochar (BMBCs700) | Tetracycline (TC) and Hg(II) | 268.3 mg/g TC and 127.4 mg/g Hg(II) | Li et al. (2020a, b) |
| Peanut hull, sugarcane bagasse, bamboo, hickory wood | Chitosan modified biochar (BB-C) | Pb$^{2+}$, Cu$^{2+}$, Cd$^{2+}$ | Sufficient adsorption | Zhou et al. (2013) |
| Cottonseed hulls | Nano MnO$_2$–biochar composites (NMBCs) | Cu$^{2+}$ | High adsorption obtained (142.02 mg/g) | Zhou et al. (2017) |
| Sugar beet tailing | SBT-biochar | Cr(VI) | Electrostatic attraction; reduction of Cr(VI) to Cr(III); complexation | Dong et al. (2011) |
| Mercury soybean stalk | Soybean [Glycine max (L.) Merr.] stalk-based biochar | Phenanthrene, Hg$^{2+}$ | Precipitation, complexation, and reduction, high regression coefficients ($R^2 > 0.995$) | Kong et al. (2011) |
| Bamboo | Biochar | Sulfamethoxazole | High adsorption capacity | Yao et al. (2012) |
| Crop residue | Biochar | Methyl violet | Complete removal of methyl violet | Xu et al. (2011) |
| Orange peel | Magnetic biochars (MOP250, MOP400, MOP700) | Naphthalene | MOP-400 showed high adsorption capacity | Chen et al. (2011a) |
| Sawdust | 400 BC and 700 BC | Pyrene | High adsorption of pyrene obtained with black carbon normalized distribution coefficients | Zhang et al. (2011) |
| Soybean stover | S-BC300 and S-BC700 | Trichloroethylene | High adsorption obtained for BC700 | Ahmad et al. (2012) |
| Peanut shell | P-BC300 and P-BC700 | | | |

### 12.4.1.3 Carbon Nanotubes

CNTs are made up of carbon layers in the form of cylindrical graphene sheets. Based on the number of carbon layers, they can be categorized as single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). The average length of CNTs is reported from 100 nm to several centimeters (De Volder et al. 2013; Mukherjee et al. 2016). Several unique properties of CNTs like high surface area, porosity, hollow and flexible structure, and lightweight make them a suitable adsorptive material (Han et al. 2016).

The conventional synthesis methods of CNTs viz. arc discharge, chemical vapor deposition (CVD), physical vapor deposition (PVD), and laser ablation methods are expensive, time-consuming, and not environmentally friendly, which create a need for some alternative green methods. In recent years, various agro-wastes such as rice husk, rice straw, sugarcane bagasse, sawdust, bamboo leaves, wheat husk, and fruits and waste leaves have been reported to synthesize CNTs. Wang et al. have synthesized CNTs from rice husk. Thus obtained CNTs were consisting of 10 μm in length and 50–200 nm in diameter (Wang et al. 2015). A group of researchers has synthesized CNTs with 50 nm diameter using wood sawdust. The process was done at 750 °C under optimized reaction conditions (Bernd et al. 2017). The reaction was performed in a designed reactor in an environmentally friendly manner. In a recent study, CNT bundles have been synthesized from rice straw via a hydrothermal process of Fe or Ni-incorporated rice straw. Thus obtained CNTs possess a high surface area with 20–70 nm of diameter (Fathy et al. 2017). Graphenated CNTs were also synthesized using rice husk as raw material via microwave irradiation method. Graphenated CNTs contain approximately 5–6 layers of graphene sheets with 50–200 nm diameter (Wang et al. 2015).

The adsorption behavior of CNTs depends on their surface area, surface active sites, and the interaction between surface active sites of CNTs and the pollutants (Duan et al. 2020). In this perspective, CNTs possess a high surface area and a large number of surface active sites which makes them a suitable candidate for adsorption (Alshahrani et al. 2021). Due to the smaller diameter of CNTs, they cannot adsorb large size particles on their surface. For that reason, it is assumed that the adsorption of pollutants can be done either at the inner side of the tube if it is in open form, or at interstitial pore spaces between the tube bundles, or outer channels of the tubes.

Alawady et al. have proposed the mechanism of metal ion adsorption on the surface of CNTs and it was assumed that when metal ions stick to the surface of CNTs it results in the release of $H^+$ ions from the surface, which decreases the pH of the solution (Refaat Alawady et al. 2020). This low pH value of the solution suggests the high positive charge on the adsorbent surface that limits the adsorption of metal ions. Liang et al. have investigated the process of metal ion adsorption on CNTs. They suggested that the adsorption of metal ions is affected by the combined effect of electrostatic attraction and sorption precipitation as well as the pH of the solution (Liang et al. 2015). Another study investigated the removal of $Hg^{2+}$ ions on CNTs and the results indicated a high adsorption amount of Hg (Gupta et al. 2014).

### *12.4.2 Metal Oxide-Based Nanomaterials*

Nanomaterials based on metal oxides have a higher ratio of surface area/volume, greater surface energy, and good interaction with support materials. They also have significant mechanical, spectral, chemical, physical, optical, magnetic properties with distinctive electronic arrangements due to the presence of several types of transition states of metals. Besides different commercial substrates like silica, alumina, clay, polymers, etc. available in the market, agro-wastes could be helpful in immobilization of metal oxide nanoparticles on their surface to produce efficient, green nanomaterials and could be utilized for wastewater treatment. Surendra et al. had synthesized ZnO nanoparticles from vegetable peel waste, *Moringa oleifera* commonly known as drumsticks, and used them in effective photocatalytic degradation of a harmful dye, crystal violet, mainly present in the wastewater effluents from textile industries. Spherical ZnO nanoparticles in the size range of 40–45 nm have degraded dye up to 94% in 70 min (Surendra et al. 2016). Another agro-waste, banana peel extracts have also been utilized to prepare ZnO nanoparticles with crystallite size in the 18–21 nm range. Here banana peel extracts were used as a source of secondary metabolites and the size of as-synthesized ZnO nanoparticles was largely dependent on their concentration. These nanoparticles are potential photocatalysts for wastewater treatment (Fernanda et al. 2021). Van and group had shown us that sugarcane bagasse and cassava root husks can be used to prepare biochar material which can be further modified by incipient wet impregnation of ZnO nanoparticles. Resultant optimized nanomaterial with 3 wt.% ZnO loading ratio showed maximum adsorption of a toxic dye, Reactive Red 24 from wastewater. This nanomaterial could also be recycled and efficiently reused up to five adsorption-desorption cycles (Van et al. 2021). In another study, rice husk ash was used as a source of agro-waste to prepare silica nanoparticles (about particles size 50 nm) which were used to remove nitrate ions from wastewater with adsorption capacity of 14.22 mg/g. Excessive use of harmful fertilizers produces nitrate-polluted water and contaminates water resources as well as soil tables (To et al. 2020). Nanosilica prepared from rice husk had been applied in the removal of organic pollutants like antibiotics from contaminated water. A polyelectrolyte, polydiallyldimethylammonium chloride was adsorbed on the surface of nanosilica which facilitates antibiotics removal, amoxicillin up to 92.3% (Pham et al. 2018). Akhayere and his fellow workers showed that barley husk waste can also be turned up to form nanosilica which was further treated with $FeCl_3$ to form magnetic silica nanoparticles further utilized in petroleum removal from wastewater. These magnetic nanoparticles with approximate ~10 nm crystallite size can adsorb 85% contaminants for 12 min and could be easily recycled up to five cycles with an overall 5% decrease in its efficiency (Akhayere et al. 2020). In another work, nanosilica has been extracted from barley and wheatgrass and a comparative study has been done in the removal of nickel(II) ions from agro-wastewater. Studies showed that nanosilica extracted from barley (>94% silica content) with 70 nm particle size adsorbed nickel(II) ions more efficiently (95%) as compared with nanosilica formed from wheatgrass (93% silica content), the particle size of approximately 100 nm which adsorbed 90% of nickel(II) ions from contaminated water. Both types of nanosilica can be reused up to eight adsorption-desorption cycles (Akhayere et al. 2019). Ultra-pure (>99%) silica nanoparticles were produced from sugarcane ash by using hydrolysis and condensation reactions, with less than 20 nm particle size and used in satisfying adsorption of harmful acid orange 8 dye from wastewater up to five cycles. These silica nanoparticles with a specific surface area of 131 $m^2/g$ effectively adsorbed more than 90% of dye from an aqueous solution (Rovani et al. 2018). Sebastian et al. mixed $FeCl_3$ solution with coconut husk in a 1:1 ratio to give rise to black colored iron oxide nanoparticles which potentially adsorbed heavy metals like cadmium and calcium from polluted water in batch biosorption experiments. Phenolic compounds present in coconut husk facilitated the adsorption of heavy metals on these nanoparticles. During the whole process, effects of various parameters like pH, adsorbent dosage, temperature, etc. were also studied. It was concluded that such green, semi-crystalline magnetite nanoparticles may be utilized in the removal of other heavy metal ions from contaminated water and could be projected as biosensors for affected water and soil resources (Sebastian et al. 2018). An economic, complex biosorbent was formed by mixing tea waste with aluminum sulfate and anionic polyacrylamide in the one pot, co-precipitation method which was proved highly effective in defluoridation of drinking water. The adsorption mechanism was suitably explained by model of Lagergren pseudo-second-order kinetics, where $OH^-$ and $SO_4^{2-}$ ions replace fluoride ions in drinking water. The fluoride adsorption capacity of this biosorbent (42.14 mg/g) was found to be higher than other prior reported biosorbents (Cai et al. 2015). Plantain or raw, green banana peel waste when treated with ferric chloride solution, formed black, $Fe_3O_4$ magnetic nanoparticles which were separated from solution by applying external magnetic field. These nanoparticles are lesser than 50 nm in size, showed very good magnetic response properties and have tremendous applications in wastewater remediation, drug delivery, biomedical fields, etc. (Venkateswarlu et al. 2013). Nanosilica extracted from corncob ash was amorphous with average diameter of about 50 nm and showed 100% efficiency in removal of a harmful dye, methylene blue, common effluent of wastewater expelled out of textile industries. As-synthesized nanosilica acted as redox catalyst in mechanism of dye removal and found to be superior in dye adsorption when compared with commercial nanosilica available in the market (Velmurugan et al. 2015). Silica nanostructures can also be extracted from olive wastes by applying alkali leaching extraction technique. These silica nanograins are highly porous, amorphous with varied particle size in the range of 15–68 nm but transformed into cristobalite, crystalline silica phase on thermal treatment at 900 °C. They have potential applications in contaminants removal from wastewater, catalysis, pozzolanic activity in cement and concrete, additives in bio-fertilizers (Naddaf et al. 2020). In a recent published work, an excellent review has been given on production of nanosilica from different wastes viz. agricultural, electronic, and industrial and then its application in wastewater remediation. Among agro-wastes various residues like sugarcane waste ash, rice husk ash, wheat straw, coconut husk ash, etc. were discussed. Different methodologies used for extraction of nanosilica from these residues were shown along with various techniques used for wastewater remediation from these silica nanostructures (Seaf El-Nasr et al. 2021).

## 12.5 Conclusion

Over the past decade, rigorous studies were carried out for the generation of nanomaterials and their applications as wastewater remediation. But still, bulk scale production of such nanomaterials has been extensively done by employing conventional techniques. Literature survey done during this work showed that greener methods like utilization of agro-waste materials, algae, fungi in preparation of nanomaterials have been limited to lab-scale. Owing to the fulfillment of 12 green chemistry principles, sustainable development goals declared by UNO, opportunities should be created in developing nations for the accomplishment of the production of green nanomaterials at an industrial scale. It will be beneficial in the advancement of nanoscience and technology, facilitate the generation of cost-effective, sustainable, less toxic, versatile green nanomaterials and provide a potential solution to the problem of agro-wastes management. The formation of green nanomaterials devoid of excessive use of harmful chemicals, templates, surfactants, thus helps in cost-cutting of the overall process, which could be a considerable factor in their mass production and industrial applications. Green nanomaterials are resistant to a higher temperature, acids, bases, have a higher surface area, excellent porosity which makes them a promising candidate to be used in the removal of various contaminants during wastewater treatment. Both academia and industries should work together to develop and promote technologies used to produce green nanomaterials out of waste materials and their further applications in wastewater remediation. This chapter summarizes various traditional methodologies used for wastewater treatment with their advantages and disadvantages, production of nanomaterials, their properties, advantages, analytical techniques used for studying morphological, structural features of nanomaterials, potential agro-waste materials used for the formation of green nanomaterials. It also outlines the utilization of such agro-waste-derived green nanomaterials in wastewater treatment. This work suggests that target-oriented, elaborative, comprehensive research is needed for large-scale production of nanomaterials by using green methods and agro-waste materials, especially the optimization of process parameters, better control on morphology, size-dependent properties of nanomaterials. Some kinetic factors, like temperature, time, and pressure should also be considered for upscaling these green methods. Thus, future experimental studies should be aimed towards an extension of lab-scale processes to industrial bulk production of green nanomaterials.

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# Chapter 13

# Removal of Organic Pollutants from Waste Water by Adsorption onto Rice Husk-Based Adsorbents, an Agricultural Waste

**Jyotirmoy Sarma, Anannya Kalita, Puspa Sharma, Mousumi Bora, and Sanchayita Rajkhowa**

**Abstract** Rice husk (RH), an agro-waste, is a fibrous material with high silica content. It is one of the largest readily available but most under-utilized biomass resources. Cellulose, lignin and silica ash are the chief elements of RH and are present in comparatively higher amounts than other biomass fuels. The rice husk ash (RHA) usually creates disposal problems. So its proper use in adsorption science as an adsorbent will be imminent. Washing/leaching of the husk followed by controlled burning can produce pure white silica. Study of surface (adsorbent) charge along with the effect of several adsorption parameters is important under adsorption science. This chapter emphasizes the application of RHA as an adsorbent for removal of several types of toxic organic pollutants (ranging from organic dyes to phenolic compounds) from waste water as a purification and remediation strategy.

**Keywords** Organic pollutants · Adsorption · Rice husk (RH) · Rice husk ash (RHA)

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## 13.1 Introduction

Reducing chemicals in water can be green and profitable

Interest in research works related to water quality improvement and preservation is growing on day by day because of its importance in sustaining life. The problem arises by the contamination of our valuable water resources at different sources. The contamination is mostly caused by continuous addition of undesirable chemicals in water resources that in turn degrades the water quality (Lvovich **1979**). Industrialization and civilization are mostly responsible for various organic pollutants in water streams. Organic pollutants, which are chemical molecules, difficult to degrade, pollute the water resources. Organic pollutants are health hazards, especially carcinogenic in nature (Yang **2011**). So their contamination can lead to serious health problems that further affect the societal health. Hence, researcher's interest increases gradually on improving the water quality and on its preservation. Researchers of different categories like scientists, academicians, governmental agencies as well as NGOs are very much concerned about the contamination of both surface and ground waters worldwide. It has been predicted that by **2050**, this contamination will lead to water scarcity for drinking purpose because of continuous increase in global population (United Nations **2011**). So, purification of water resources and suppliers is an utmost need with respect to the elimination of poisonous impurities.

### *13.1.1 Efficacy of Adsorption Technique in Waste Water Treatment*

In general elimination of organic contaminants from waste water has been performed by numerous treatment technologies based on bio-physical and chemical processes like bio-oxidation, reaction with oxidants (e.g. $O_3$ or $H_2O_2$, etc.), oxidation/degradation by photo-catalysis (Ahmaruzzaman and Gayatri 2010), membrane processes (Altınışık et al. 2010), electrochemical oxidation/degradation (Ahmed et al. 2014) and adsorption process. Comparatively, applicability of adsorption technology is noteworthy among all methods because of its low operation cost, easiness in operation, tactlessness to poisonous impurities and high productivity and efficacy (Ahmad and Alrozi 2011). Even adsorption process is effective in removing organic pollutants of both soluble and insoluble forms, interestingly with zero hazardous by-products production. Hence purification of waste water can be achieved effectively by adsorption of various impurities/contaminants. Adsorbents (surface or interface) play a significant role in adsorption. Commonly activated carbons are considered as best adsorbents for waste water treatment because of their higher adsorption capacities and hence widely used. However, considerably high production and regeneration cost of activated carbons make them less economically viable as an adsorbent. Therefore, the demand of agricultural waste materials is very high for application as adsorbents during waste water treatment. Rice husk (RH) and its ash (RHA) which are by-products of rice milling industries are good example of low-cost adsorbents.

### *13.1.2 Importance of Agricultural Wastes as Adsorbents*

The purification of polluted water with activated carbon based materials via 'adsorption' dates back to the year 1940 (Cheremisinoff and Ellerbusch 1979). But activated carbon is not economically viable and hence restricts its uses at large scale. Alternatives of activated carbon can solve the problem. Accordingly researchers had been working towards the development of low-cost adsorbents (Srivastava et al. 1987; Ali 2011). In this regard the use of agricultural waste products can solve dual problems. One that, it can generate low-cost adsorbents and secondly the recycling of wastes concept fulfils by the waste minimization, recovery and reuse (Patteson 1989). A series of works on utilizing agricultural wastes for preparing adsorbents, particularly activated carbon, to remove organic toxins such as textile dyes and pesticides are available in literature (Demirbas 2009; Rafatullah et al. 2010). Nevertheless removal of contaminants like organic pesticides, dyes, phenolic compounds and polynuclear aromatic compounds via adsorption process with low-cost biosorbents, primarily lignocellulosic materials is also significant (Tran et al. 2015. Agricultural waste adsorbents can be used as such or in various forms like ash, reformed agricultural waste or as prepared activated carbon for waste water treatment. It is indeed an important information that a range of waste materials viz. clays, red mud, zeolites, sediment and soil, waste metal oxides from mineral processing plants, food wastes, coconut shell, sawdust, rice husk, petroleum wastes and fly ash can be utilized as source of adsorbents for waste water treatment.

### *13.1.3 Composition of Agricultural Wastes*

Agricultural wastes have three main structural components, i.e. lignin, cellulose and hemicellulose (Salleh et al. 2011. Lignin possesses a complex three-dimensional structure, made up of polymeric aromatic ring. The various functional groups (such as hydroxyl and carboxyl) attached to the aromatic rings in lignin play the key role during their reactions (e.g. adsorption). Besides, hemicellulose and cellulose are basically soluble in basic medium and also effortlessly hydrolysed because of their oxygen containing functional groups such as hydroxyl, ether and carbonyl (Chowdhury et al. 2011). These functional groups as mentioned previously are primarily responsible for the adsorption processes.

### *13.1.4 Characterization of Waste Water*

Contaminated water generally has unpleasant odour and deteriorated colour. However, several physicochemical parameters govern the quality of waste water. Among these, chemical oxygen demand (COD) and biological oxygen demand (BOD) are significant as they can suggest about the biodegradability of the organic pollutants in waste water. Generally higher COD than that of BOD value indicates slower biodegradability of pollutants in waste water (Qasim and Mane 2013). Moreover, alkalinity and electrical conductivity measurements also provide valuable information about the nature of contaminants. During characterization of waste water, the amount of chlorides along with surfactants is generally monitored for their adverse effects in living beings. Generally they must be within a permissible limit. Apart from all these, total suspended and dissolved solids are also important parameters for characterizing waste water.

### *13.1.5 Persistent Organic Pollutants (POPs)*

Organic pollutants also referred to as POP belong to the category of toxic chemicals that affect the human health and also pose threat to the environment because of their easy transportation via wind and water. These pollutants can persist in the environment for comparatively longer time period and they can accumulate from one species to the other thereby contaminating the food chain. The persistent organic pollutants are sometimes referred to as 'forever chemicals'. These toxic chemicals are organic compounds that are resistant to environment degradation through the photolytic, biological and chemical processes (Shatalov et al. 2004). Due to their persistent longer lifetime, these POPs can bio-accumulate and pose adverse impact on the environment as well as on human health. These are the toxic substances that constitute several organic chemical mixtures and industrial chemicals like polychlorinated biphenyls (PCB) and pesticides like DDT. These toxic products and by-products are mainly obtained from chemical manufacturing and industrial processes. The organic pollutants mainly constitute the phenols, azo dye, polyaromatic hydrocarbons, pesticides, polychlorinated biphenyl, chlorinated phenols, and endocrine disrupting chemicals while the inorganic pollutants constitute variety of toxic heavy metals like chromium (Cr), arsenic (As), mercury (Hg), lead (Pb), cadmium (Cd), etc. (Shatalov et al. 2004).

The escalation of industrialization leads to significant increase in the distribution of these toxic substances and the other non-biodegradable pollutants from the industrial waste water to the surroundings. Among these contaminants, the POPs were found to be detrimental to the humans as well as flora and fauna. Thus in order to resolve this problem, the interest in waste water treatment has augmented over the last decades. These toxic compounds can be removed from the environment most effectively by the application of adsorption processes with low-cost adsorbents like activated carbon (Kumagai et al. 2009).

### 13.1.6 Organic Pollutants in Waste Water and Their Toxicity

Waste water contamination is one of the major concerns of environmental pollution. This is mainly due to the intensification of industrialization (food, petrochemical, pharmaceutical, rubber, leather, plastic paper, dye and textile industries), agricultural activities (use of pesticides in agriculture, forestry, aquaculture, veterinary), municipal sewage, and other environmental changes (Djilani et al. 2012. Such contaminations can lead to intricacies like mutagenicity, teratogenicity, carcinogenicity and embryotoxicity. Other health-related disorders of human body include the dysfunctioning of the central nervous system, brain, reproductive system, liver and kidney (Salman et al. 2011). Several review studies are carried out related to such information (Aksu 2005; Ali 2011) but still no effective measures are being adopted for the removal of these organic pollutants. The different kinds of organic pollutants found in water bodies constitute the hydrocarbons plasticizers, biphenyl, detergent, oil, pharmaceuticals, grease, heavy metals, pesticides, fertilizers and phenols (Damià 2005). Such organic pollutants pose several side effects and it has been cited by world health organization (WHO report 2010). These organic pollutants consist of fused non-polar carbon rings with various kinds of substituents. These organic pollutants are considered as persistent pollutants in the environment because of the deficiency of polar functional groups in their structure (Shatalov et al. 2004). Thus with growing importance of water quality and its environmental aspect the use of low-cost adsorption techniques for the removal of organic pollutants from waste water has attained much recognition. The present chapter outlines the treatment of waste water by adsorption of such pollutants on rice husk (RH) based adsorbents.

## 13.2 Development of Rice Husk-Based Adsorbents

### 13.2.1 Rice Husks (RH)

Rice husk is the major by-product of the rice milling industries. It is the protective outer shell of the rice grain. It has been considered as abundant material because of large annual production across the world (Chandrasekhar et al. 2003). Annually the husk production is one-fifth part of the rice production worldwide. Consequently the discarding problem of husk evolves. RHs are basically lingo-cellulosic materials composed of 32% cellulose, 21% hemicelluloses, 21% lignin, 20% silica and 3% crude protein (Real et al. 1996). Presence of certain reactive functional groups like carboxyl and hydroxyl makes rice husk an efficient adsorbent.

Rice husk (RH) is an abundant agricultural waste for generation of low-cost adsorbents. However, quality of synthesized adsorbents is dependent upon the 'precursors' and 'processing methods'. Generally inexpensive and non-hazardous precursors are applicable in this context provided they are freely available. Besides, the adsorbent groups should be abundant in carbon or oxygen content for having good adsorption results. Physical characteristics of precursors such as small pore size with higher surface area are also important for enhanced adsorption activities. The origin of precursors may be organic or inorganic. The organic precursors are rich in carbon content. For example, the agricultural waste, rice husks (RH) are a kind of organic precursor. Certain characteristics like rough fibre geometry, insolvability in water, good mechanical stability and strength, and its abundancy make rice husk a suitable adsorbent material (Amutha et al. 2010). The inorganic precursors mostly consist of the earth crust materials like soil and clay. The generation of low-cost adsorbents (so called 'activated carbons') from organic precursors depends upon carbonization and activation. Hence these are also called as processing methods. Activation can be achieved by physical or chemical treatments. Moreover, modification of agricultural wastes is also significant for improving its adsorption properties. Several methods including acid or alkali treatment, etherification, esterification and other modification are known. For example, rice husk (RH) was modified by mild alkaline hydrolysis (NaOH) for enhancing adsorption properties (Kalapathy et al. 2000).

### *13.2.2 Rice Husk Ash, 'RHA'*

Rice husk, an agro-waste material, acts as source of amorphous silica. Silica is generally used as filler materials, catalyst support, adsorbent and a silicon source because of its high mechanical strength. The ash recovered from RH, so called RHA might be associated with various impurities like metal ions and unburnt carbon that generally influences the performance of the material as adsorbent. Removal of such ions prior to burning of the husk can produce white silica of high purity. RHA is abundant in amorphous silica. The silica content in 'RHA' is 85–95% of amorphous form, whereas it is 17–20% in 'RH' (Chandrasekhar et al. 2003). Dumping of RHA can cause damage to the land and so considered as an environmental threat. A typical snapshot is shown in Fig. 13.1.

The silica ($SiO_2$) in the RH can be found mostly in its hydrated amorphous form like silica gel. Highly porous and amorphous silica can be obtained by thermal degradation and pyrolysis of RH, but with some unburnt carbon as impurity (Kapur et al. 1985). Combustion of the 'RH' at moderate temperature results in the formation of white ash, with approximately 92–97% of amorphous silica and also some metallic impurities. However, these can be further removed by acid/alkaline leaching treatments followed by calcinations at high temperature. Acid leaching of the husk can produce pure silica with high surface area. The chemical composition of

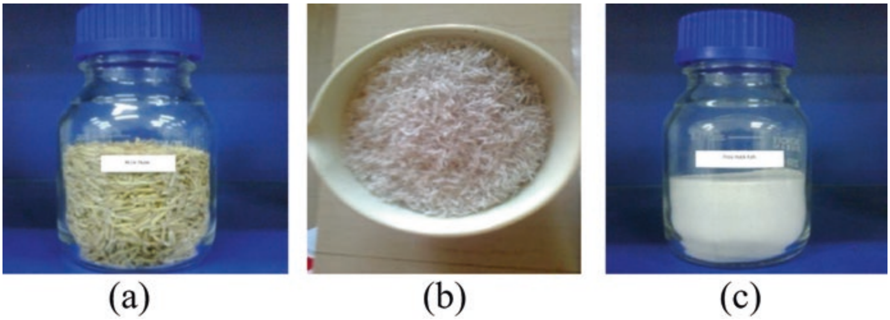

Fig. 13.1 Photographs of (**a**) Rice husk (**b**) Rice husk ash (**c**) Rice husk silica powder

**Table 13.1** The chemical composition of RHA (mineral ash) (modified based on 'Banerjee et al. 1982')

| Various oxides | RHA as received | RHA after combustion |
|---|---|---|
| $SiO_2$ | 72.1 | 94.95 |
| $Al_2O_3$ | 0.30 | 0.39 |
| $Fe_2O_3$ | 0.15 | 0.26 |
| CaO | 0.43 | 0.54 |
| $Na_2O$ | 0.50 | 0.25 |
| $K_2O$ | 0.72 | 0.94 |
| MnO | 0.15 | 0.16 |
| $TiO_2$ | 0.05 | 0.02 |
| MgO | 0.70 | 0.90 |
| $P_2O_5$ | 0.06 | 0.74 |
| Loss on fire | 24.3 | 0.85 |

rice husk ash before and after burning out at 700 °C for 6 h is shown in Table 13.1 (Banerjee et al. 1982).

Interestingly, the composition of RHA is dependent upon certain factors like paddy variety, part of moistened area, environmental conditions, fertilizers, weather and climatic change, earth chemistry and agricultural activities (James and Rao 1986).

More specifically, burning of rice husk below 700 °C results in the formation of amorphous rice husk ash. The amorphous rice husk ash or silica ash is suitable as adsorbent because of its fine particle and pore size. However, high reactivity of silica ash is also attributed to the presence of surface hydroxyl groups. The formation of amorphous white (low-carbon) silica ash is dependent on combustion time and temperature of the husk (Chakravarty et al. 1988). Highest amount of amorphous silica results by the combustion of 'RH' at a range of 500–700 °C, and at greater temperatures, crystalline silica is formed. However, structural transformation of amorphous silica to crystalline phase occurs on thermal treatment at varying temperature range. High temperature (800 °C) combustion leads to melting of silica framework with carbon fixation. Moreover, burning of samples of rice husk at 750 °C or above can result into environmental pollution because of crystallization (Krishnarao et al. 2001). Hence controlled burning of RH can produce reactive silica with suitable adsorbent characteristics.

### *13.2.3 Characterization of RH and RHA*

RH is a kind of lignocellulosic material that composed of cellulose, hemicellulose and lignin. The chemical composition of RHA has also been mentioned previously (Table 13.1). RHA is suitable as an adsorbent material because of its important characteristics. The energy dispersive X-ray (EDX) spectroscopic analysis of 'RHA' confirms the presence of 'silicon' as the most abundant element. Scanning electron microscopic (SEM) along with tunnelling electron microscopic (TEM) techniques help in understanding the morphological characteristics of 'RH' and 'RHA'. Generally, the irregular surface of rice with many cavities having different pore sizes makes them a good adsorbent. Nevertheless, the occurrence of functional groups like carboxyl (-COOH) and silicon alcohol (-Si-OH) on 'RH' and 'RHA' are chiefly accountable for the adsorption phenomena (Srivastava et al. 2006). The presence of these characteristic functional groups can be confirmed by Fourier transform infrared (FTIR) technique. Moreover, X-ray diffraction (XRD) analysis also confirms the presence of 'quartz' as the solitary crystalline phase available in RHA (Jauberthie et al. 2000).

### *13.2.4 Brief Applications of RH Based Adsorbents*

Rice husks and its ash (RHA) are abundant and cheap adsorbents worldwide. Rice husk carbon (RHC) was studied for application as adsorbent in water purification contaminated with methylene blue (Tannin and Gurgey 1988). RH based low-cost adsorbents were found more effective in removing industrial textile dyes than that of costly granular commercial carbon. Also the overall processing cost with rice husks as adsorbents is comparatively cheaper than that with commercial carbon based adsorbents. Rice husk (RH) based adsorbents is effective in removal of various organic dyes and other types of pollutants (Guo et al. 2003; Kumagai et al. 2009). Chemical activation of RH based adsorbents for enhancing adsorption capacity is an effective process. However, rice husk ash (RHA) uses its surface functional groups for uptaking the heavy polluting metals from waste water via adsorption (Srivastava et al. 2006). Carbon and silica are mainly responsible for adsorption of RH adsorbents. Rice husk along with its ash are beneficial as adsorbents because of their low production and regeneration cost. Moreover, RH based adsorbents are promising candidate in the waste water treatment as are less-expensive material and also it solves the disposal problem.

## 13.3 Adsorption Study

Fundamentally, adsorption involves the uptake of atoms and molecules by some material surfaces. Accordingly during waste water treatment, removal of wastes is achieved by adsorption onto various adsorbents. The chemicals present in waste water are considered as adsorbates and the adsorbing phase being the adsorbent. However, the term ‘bio-sorption’ is more suitable in case of bio-adsorbents like rice husk.

### *13.3.1 Adsorption Kinetics*

Adsorption kinetics study in adsorption science is significant as it provides information about the adsorption equilibration time or surface (adsorbent) saturation time. The equilibration time is dependent upon the types of adsorbates/adsorbents used and other experimental conditions like pH and temperature (T) of the reaction. Such kinds of information are important for selection of adsorbents in decontamination of polluted water. The adsorption rate predicts the applicability of adsorbents in industrial processes as an adsorbent and the adsorbate get the chance of interaction for only a limited period of time. Generally, a sorption process consists of the following steps:

1. Transport of a substance from the bulk solution to the surface.
2. Diffusion of adsorbate into pores of the surface.
3. Adsorption of a substance onto the surface by favourable interaction.
4. Desorption of the adsorbate from the surface.

The role of rate determining step (r.d.s) is essential for predicting the speed of the reaction. Generally, slowest step, amongst all, is considered as rate determining step. Kinetic equations with respect to the r.d.s are developed and fitted to the experimental data. The adsorption kinetics is associated with two stages, a rapid uptake stage surveyed by a comparatively slower stage before the attainment of equilibrium. Theoretical kinetic models of both first and second orders, with their linear and non-linear forms, are applied for simulation of the experimental kinetics data. The Lagergren’s kinetic model was not successful for justifying experimental data at high surface saturation times. However, the application of Lagergren’s first-order equation and the pseudo-second-order equation of linear form is limited over the pseudo-second-order equation of non-linear form during adsorption (Sarma and Mahiuddin 2014; El-Said 2010; Safa and Bhatti 2011a) (Table 13.2).

**Table 13.2** Common adsorption kinetics and isotherm models (Source: modified based on Sarma and Mahiuddin 2014)

| Kinetics models | Equation | parameters |
|---|---|---|
| Lagergren first order | $\frac{dq_t}{dt} = k_1\left(q_e - q_t\right)$ | $q_e$ and $q_t$ are the amount of an adsorbate adsorbed onto an adsorbent at equilibrium and at time, $t$ and $k_1$ is the first-order rate constant |
| Pseudo first order | $\text{In}(q_e - q_t) = \text{In}q_e - K_1t$ | Do |
| Pseudo second order (linear) | $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ | $q_e$ and $q_t$ are the amount of an adsorbate adsorbed onto an adsorbent at equilibrium and at time, $t$ and $k_2$ is the second-order rate constant |
| Pseudo second order (non-linear) | $q_t = \frac{q_e^2 k_2 t}{q_e k_2 t + 1}$ | |
| Isotherm models | | |
| Freundlich | $\log q_e = \log K_f + n\log C_e$ | $C_e$ and $q_e$ are the equilibrium concentration and amount of adsorbate adsorbed respectively, $K_f$ is the Freundlich co-efficient representing adsorption capacity and $n$ is the adsorption intensity, $n < 1$ represents favorable adsorption |
| Langmuir | $\frac{1}{\Gamma} = \frac{1}{\Gamma_{\max}} + \frac{1}{\Gamma_{\max} C_e K_L}$ | Where, $C_e$ is the residual concentration of adsorbate, $K_L$ is the adsorption co-efficient, $K_L = K_a/K_d$, $K_a$ and $K_d$ are the rate constant for adsorption and desorption respectively. $\Gamma$ and $\Gamma_{\max}$ are the concentrations of an adsorbate per unit area of an adsorbent at equilibrium and after saturation of the adsorbent surface respectively |

### *13.3.2 Adsorption Isotherms*

Study of the batch adsorption processes at a fixed temperature with other variables helps in understanding the adsorption mechanism for an adsorbate-adsorbent couple. Frequently the application of Langmuir and Freundlich isotherm models is popular in adsorption science. These adsorption models are very much applicable in adsorption with rice husk (RH) and ash too. In addition to this, isotherm models like Redlich–Peterson, Dubinin–Radushkevich (D-R), Temkin, Toth, Sips, Frumkin, Harkins-Jura (H-J), Halsey and Henderson isotherms, also found effective applications. The Langmuir and Freundlich isotherms are advantageous over others as are applicable during adsorption equilibrium (Bhattacharya et al. 2006). The Langmuir and Freundlich isotherm models are presented in Table 13.2. Moreover, study of adsorption isotherms at different temperatures helps in providing information about thermodynamic parameters like Gibb's free energy, enthalpy (heat) and entropy for adsorption processes. Thermodynamics in turn helps in predicting the spontaneity of adsorption reactions.

### *13.3.3 Mechanism of Adsorption*

The mechanism of adsorption has its own set of challenges and before understanding the mechanism of adsorption, the structure of the adsorbate and the surface property of the adsorbent must be understood. Several processes like the FTIR spectroscopy, X-ray diffraction (XRD), attenuated total reflection (ATR), SEM, TEM, EXAFS, electrophoretic mobility (EM), etc. are used for studying the mechanism related to adsorption. Several other types of interactions like H-bonding (hydrogen), chemisorption and ion exchange are used to study the adsorption but amongst them, chemisorption portrays the chief mechanism for adsorption of organic pollutants (Chowdhury et al. 2011). Based on these type of interactions, different surface complexation models like inner-sphere and outer-sphere are usually proposed for explaining the adsorption mechanism.

The adsorption of the organic pollutants onto the adsorbent is controlled by the physical forces like the Van der Waals force, hydrogen bonding, polarity and steric interaction, π–π interactions and the dipole induced dipole interaction or their combination (Chakraborty et al. 2011. However in the chemical adsorption mechanism, sharing of the electrons takes place between the pollutants and the surface of the adsorbent resulting in the formation of a chemical bond. Apart from this, the film diffusion and particle diffusion models are also often used for studying the diffusion mechanism.

During the physical adsorption process, the pollutants get adsorbed onto the adsorbent surface by the above-mentioned mechanisms. For example, the adsorption of dye onto the surface of NMRH (sodium hydroxide modified rice husk) may be due to the formation of surface hydrogen bonds between the hydroxyl groups on the NMRH surface and the nitrogen atoms of the dye crystal violet (CV) as shown in Fig. 13.2 (Chakraborty et al. 2011. The oxygen/nitrogen carrying groups of the adsorbate form hydrogen bonds with the polar hydroxyl groups of adsorbent. The researchers also investigated the chemical interaction between the adsorbate and the adsorbent to study the chemical adsorption process. It was also investigated about a complex method of removal of pollutants like methylene blue and malachite green by adsorption onto the raw and reformed rice husk (RH) via ion exchange (Foo and Hameed 2011. The removal process consisted of both the surface adsorption and the pore diffusion mechanisms. It has been confirmed about the involvement of chemisorption mechanism during adsorption of the direct dyes like Direct Red-31 and Direct Orange-26 onto the rice husk apart from the diffusion mechanisms (Safa and Bhatti 2011a).

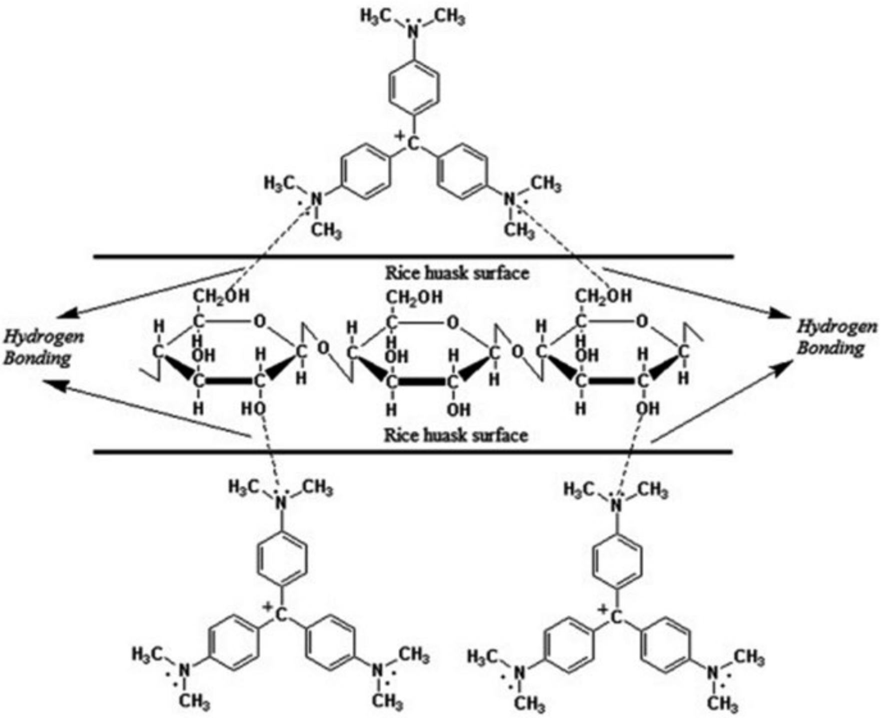

**Fig. 13.2** Adsorption of CV onto NMRH (Source: Chakraborty et al. 2011)

### 13.3.4 Regeneration of Adsorbent or Desorption Studies

Regeneration of the adsorbents includes several different techniques like the thermal regeneration (steam and hot water), chemical regeneration process. The regeneration of adsorbents is primarily used during the waste water treatment for reducing the processing cost and recovering the adsorbates. This also helps in understanding the adsorption mechanism. In the chemical desorption process, the selection of the desorbents (including organic desorbents like methanol, ethanol, acetic acid or a combination of both and the inorganic desorbents like HCl, NaOH, $H_2SO_4$) and suitable pH are highly important (Sathishkumar et al. 2012. The feasibility of any adsorption system depends on the disposal or the regeneration of the spent adsorbent. The rice husk (RH) being primarily cellulosic and carbonaceous are advantageous as adsorbents owing to their low production cost and they can also be easily disposed by means of drying, burning and dewatering. The heat of combustion that is produced as waste heat can be used for demoisturizing the adsorbent and steam production. Reutilization of the adsorbent like (RH) and recovery of the adsorbed materials can be achievable by the desorption mechanism. The desorption treatment can either improve or in some cases retard the efficacy of the adsorbents. In the continuous flow systems, the adsorption and desorption processes take place without much intrusion (Jain et al. 2004). Various desorbents (like acids, alkalies) may be used depending upon the adsorbates, economic reasons and processing requirements. Selective desorption is also applicable for some metals. In the context of recovery of rice husks as adsorbents, organic solvents like methanol and ethanol play a significant role as desorbents. Moreover, the organic pollutants like pesticides and phenolic compounds can be desorbed by the use of deionized water, $CaCl_2$ and NaOH (Gupta et al. 2000).

## 13.4 Adsorption of Organic Pollutants Onto Rice Husk-Based Adsorbents

### *13.4.1 Adsorption of Organic Dyes onto RH and RHA*

Organic dyes are major precursors in dyestuff manufacturing industries and the textile industries. Dyes are emitted into the water bodies from such industries. Most such type of dyes are commonly used in textile and rubber productions as well as in printing, petroleum and paper factories (Saquib et al. 2008; Vimonses et al. 2009). Industries like rubber, textiles, plastics and cosmetics have wide use of dyes as colour imparting agents, which are again generalized as industrial wastes. The contamination of dyes to water bodies during manufacturing and dying processes is a matter of serious threat to the environment. Because they can impose toxic effects on the microbial populations and are considered to be carcinogenic to mammalian animals. The organic dyes are very poisonous chemical compounds with complex chemical structures. The presence of these compounds in water reduces diffusion of light into water. This in turn affects the photosynthesis of aquatic plants and thereby creates toxicity to living organisms in water. Hence aquatic life is affected and also propagated to long distance or globally. Because of the complex aromatic structure, the degradation of organic dyes is difficult (Gupta 2009). They do not undergo aerobic digestion and so are not biologically degradable. Hence purification of water bodies from organic dyes becomes a matter of concern. The common physicochemical treatments adopted for removal of dyes from waste water include adsorption, advance oxidation process (AOP), membrane separation via coagulation and flocculation (Poots et al. 1976). However, adsorption technique is found superior for treatment of dye-containing waste water, amongst the various techniques, especially if some inexpensive adsorbent is used which don't require additional pre-treatment before its application. In this context, RH and RHA play substantial role as inexpensive adsorbents. RH serves as good adsorbent material because of its superior chemical stability, high mechanical strength, granular structure and most importantly is insoluble in water. Knowledge about the chemical structure of RH and RHA is very important for understanding the adsorption process. Spectroscopic characterization like FTIR (Fourier transform infrared) technique can help in structure determination of RH. Moreover, chemical modification of RH improves its adsorption capacities by the incorporation of functional groups such as carboxyl and silanol.

Various experiments were carried out by allowing adsorption of various dyes on rice husk (RH), modified rice husk and rice husk ash (RHA). Obviously, all dyes were found to have different adsorption capacities. However at equilibrium, there was no noticeable effect observed of amount of dye used, reaction speed, pH, and ionic strength on the percentage dye removal. Moreover, thermodynamic parameters play significant role in determining the feasibility of an adsorption process. For example, a feasible and spontaneous adsorption of the dye 'Indigo Carmine' (IC) onto RHA was seen after calculating some thermodynamic parameters such as entropy change, ($\Delta S^0 > 0$), the heat of adsorption ($\Delta H^0$) and the change in Gibbs free energy ($\Delta G^0 < 0$) (Lakshmi et al. 2009). Application of adsorption isotherm models such as Langmuir and Freundlich at varying temperatures helps in finding out the different thermodynamic parameters. In addition, increase of reaction temperature also favours the uptake of dyes like Brilliant Green (BG) onto rice husk ash (RHA). At the same time the favourable change in free energy ($\Delta G^0$) also favours the adsorption of BG upon RHA (Mane et al. 2007). Alkaline modification of rice husk (RH) with NaOH was found to be pH dependent during the adsorption of dye 'BG' onto RHA. Moreover, the adsorption process is endothermic in nature, which is confirmed by the direct dependence of rate constant upon temperature. The mechanism of adsorption being the chemical ion exchange between the heterogeneous surface of rice husk and adsorbates.

Studies on the application of adsorption process on dye removal is interesting and essential. The colour of a range of dyes, e.g. acid violet, acid blue, acid red, methylene blue, congo red and brilliant blue, can be reduced from their aqueous solution using rice husk ash (RHA) as an adsorbent (Kermani et al. 2006a, b). In fixed-bed column adsorption process, removal of dye like Brilliant Blue FCF was achieved by penetration of the dye molecules through the bulk of the column containing RHA as adsorbent then followed by determination of percentage saturation of the columns. The dyes can be recovered by alkaline elution of the solution. The adsorption process is found to be governed by diffusion-controlled mechanism of the adsorbates (Gupta et al. 2006). However in overall, the kinetically controlled phase is 'mass transfer step' followed by diffusion.

Structural modification of adsorbent also enhances the adsorption of dyes. The adsorption of direct red (DR) and direct orange (DO) onto rice husk (RH) causes structural changes of the surface, which was confirmed by SEM technique. Their adsorption follows Langmuir adsorption behaviour. On the other hand, removal of Neutral Red (NR) was performed by acid treated rice husk (MRH) and confirmed by diffusion. However, intra-particle diffusion was not the rate-controlling step. Spectroscopic technique confirms enhanced adsorption of 'NR' onto modified rice husk (MRH), done by functionalization with carboxylic groups (Zou et al. 2009). At the same time, malachite green (MG) was removed effectively by phosphoric acid ($H_3PO_4$) and sodium hydroxide (NaOH) modified rice husk. It has been noted that adsorption of MG is favourable on carbon-rich sites of rice husk (RH) than that of the silica-rich sites. The silica content of RH results in decrease in adsorption of malachite green. Moreover, the applicability of adsorption isotherm models depends on the nature of modification of adsorbent surfaces. At the same time, rice husk modified with reagents like carboxymethyl cellulose (CMC) and poly vinyl alcohol) (PVA) results in effective adsorption of organic dyes from polluted water (Safa and Bhatti 2011b). The adsorption isotherm results were validated by Langmuir Type I and Type II models.

### *13.4.2 Adsorption of Detergents and Oils*

Detergents are surfactants that can reduce the surface tension of water when they are used at extremely low concentrations. They consist of an amphiphilic structure where each of the molecules has an hydrophilic head and a long hydrophobic tail. The detergent molecules can aggregate to form micelles that makes them soluble in water (Rajkhowa et al. 2017). The detergents comprise of about 35–75% of phosphate salts that can lead to fresh water algal blooms and reduce the amount of dissolved oxygen in the water bodies (Ni et al. 2018). There are three types of surfactants—ionic, non-ionic and the amphoteric. The examples of the ionic surfactant include the sodium alkyl sulfonates that are used in wide range of detergents, dishwashing liquids, shampoos and shaving foams. The sodium dodecyl benzenesulfonates $C_{12}H_{25}C_6H_4\text{-}SO_3Na$ is a common laundry detergent and the anionic surfactants. Linear alkyl benzene sulfonates (LABS) are very toxic to the aquatic and the terrestrial ecosystems. Several processes like membrane technology, chemical precipitation, photocatalytic degradation, etc. are used for the removal of detergents from the water but the adsorption is the best known purification method for the removal of the surfactants (Nguyen et al. 2018). The activated carbon based adsorbents were prepared by the water vapour pyrolysis of olive stones, peach stones, natural asphaltite, mixture from coal tar pitch and furfural. They exhibit strong adsorption towards the phenolic and the sulfonic compounds and they mainly depend on the surface chemistry and porous parameters. (Tsyntsarski et al. 2014).

Fats and oils are called the triglycerides because they are esters comprising of three fatty acids joined to glycerol, a trihydroxy alcohol. This triglyceride is called as oils and it remains as a liquid at a temperature of 25 °C. The several sources of oil pollution include the discharge of the untreated municipal sewage into the water sources, untreated waste water from the coastal industries, accidental or operational discharges of the oil from the refineries, oil storage tanks, oil terminals and the emission of the gaseous hydrocarbons from the oil handling onshore facilities and the vehicle exhausts (Yang et al. 2015). The increasing rates of oil spills in the seas and oceans can choke the aquatic life to death and can also increase the overall temperature of the sea/ocean water that can pose threat to the exotic aquatic flora and fauna. Thus the use of efficient and low-cost adsorbents can eradicate this problem.

The amount of linear alkyl benzene sulfonate (LABS) in raw domestic waste water lies in the range of 0.54–21 mg/L (Weeks et al. 1996). So there exists an utmost need for the removal of LABS kind of surfactants from water bodies as it imposes severe threats to the aquatic lives even at a concentration of 0.1 mg/L. Quarternized rice husk (QRH) is also an effective adsorbent for surfactants removal over non-modified one. Interestingly, the adsorption of the detergent 'linear alkyl' is temperature dependent up to certain point, followed by an adsorption plateau indicating adsorbent surface saturation. Nevertheless, for surfactants removal from waste water, rice husk and RHA play a significant role as low-cost adsorbents (Hosseinnia et al. 2006). However for surfactant adsorption, the micellar size and the critical micellar concentration (CMC) along with other physicochemical characteristics of the RH are found to be important properties affecting the adsorption processes. There exists resilient van der Waals (V-W) forces amongst long chains of surfactant and the cellulose from RH, which are believed to be responsible for the adsorption.

### *13.4.3 Adsorption of Pesticides, Herbicides, Pharmaceuticals and Fertilizers*

Modern intensive agriculture relies heavily on pesticides. As a result of their leaching and atmospheric deposition, these agro-based components have contaminated groundwater and surface water reserves. Most of the widely used pesticides have been resistant to environmental degradation, posing health risks for humans and environmental toxicity concerns (Grover and Cessna 1990). Herbicides are suspected mutagens and carcinogens and may be toxic to living organisms, which are widely used during plant growth regulators in agriculture and non-agriculture. As a result, it really does have the chances to be toxic to living organisms, causing chronic nervous system injuries, nausea and dizziness, and coughing after inhalation (Crespin et al. 2001). Pharmaceutical industry emission of APIs from industrial production is referred to as 'pharmaceutical toxic waste'. Drug companies in Hyderabad, India, were found to be emitting high levels of pharmaceuticals, according to a paper published in 2007 (Larsson et al. 2007). River sediment, surface and ground water as well as the drinking water have been polluted due to increased levels of contaminants from pharmaceutical products, i.e. penicillin (Li et al. 2008). Agricultural fertilizers are chemical compounds used to increase the productivity of crops. In order to achieve maximum crop yield, farmers use these on a daily basis. The disadvantages of fertilizers are: They are expensive. The fertilizer's ingredients are harmful to the skin and respiratory system. An overabundance of fertilizers damages the plants as well as drastically reduces the soil's fertility. As a result of leaching, the fertilizers end up in the rivers and cause eutrophication. Use over a long period of time significantly decreases the microbial activity and alters the soil's pH.

#### 13.4.3.1 Adsorption of Pesticides

Pesticides being removed from the environment became one of the world's biggest environmental concerns today. Chemical waste water treatment entails a series of chemical reactions which really help hydrolyse contaminants and convert them to safer chemicals. Several bio-purification systems (BPS) have been developed to treat pesticide-contaminated waste water with microorganisms that can digest pesticides. The use of membrane filtration methods in waste water treatment plants is becoming more and more common. Based upon this membrane types as well as the target contaminants, filtration is being at any phase during the water treatment. Rice husk (RH) is used to remove pesticides from groundwater. Only a few of research findings on pesticide removal from domestic waste water have been published. The uptake of 'paraquat' from aqueous phase by applying rice husk improved with methacrylic acid, was found effective (Hsu and Pan 2007). Grafting of the RH chain with Fenton's reagent as a redox activator enhances its adsorption capacity. Adsorption was fast during the first few minutes as well as reached equilibrium instantly in this study. It has been reported that RH has the potential to remove methyl parathion pesticide (MP) from groundwater and surface water (Akhtar et al. 2007). According to this study, exothermic and spontaneous phenomenon of adsorption was revealed by the negative numbers of the thermodynamic properties of the adsorption mechanism ($\Delta H$, $\Delta S$, and $\Delta G$). It is possible to remove pesticides from sorbents by sonicating (ultrasound-assisted) them in the presence of methanol. The removal of seven types of pesticides (alachlor, metolachlor, fipronil, chlorpyriphos, a-endosulfan, b-endosulfan and p-p′-DDT) as well as two of their by-products (p, p′-DDE and endosulfan sulphate) from waste water was also investigated by rice husk ash (RHA) (Saha et al. 2014). As a result, it can be inferred that RHA is being used as a low-cost adsorbent for the effective removal of pesticides from readily available polluted water.

Conversely, due to the increasing price and scarcity of frequently used costly adsorbents like activated spent bleaching earth (SBE), layered double hydroxides (LDHs) organic polymer resin Lewatit VP OC 1163, goethite and humic acid-coated goethite (Iglesias et al. 2010), etc., extraction of emerging, cost-effective and traditional waste products for pesticide removal from industrial waste water is the focus of many researchers. The previous studies also show how RHA is produced from agricultural residues rice husk, that farmers and commercial rice mills often have trouble disposing of. RHA is considered as an emerging cost-efficient adsorbent for an effective removal of dispersed pesticides from waste water due to its abundant availability of agricultural residues as well as the relatively inexpensiveness of preparation.

#### 13.4.3.2 Adsorption of Herbicides

Chlorophenoxy herbicides are found in a wide range of commercial products. The skin, eyes, respiratory and digestive linings can be slightly irritated by chlorophenoxy acids, salts, and esters extensively in various cases. There are a few findings of peripheral neuropathy mostly in medical literature, most of these approaching dermal exposures to 2,4-D as well as another following uptake (O'Reilly 1984). They are weak decouplers of phosphorylation, so they can cause hyperthermia by enhancing the levels of body heat. The bio-sorption of 2, 4-dichlorophenoxyacetic acid (2, 4-D) herbicide in some kind of a fixed-bed column system using rice husk (RH) based biochar was also investigated (Bahrami et al. 2018). The effects of pH (2, 5, 7, 9), flow rate (0.5, 1, 1.5 mL $\text{min}^{-1}$), bed depth (3, 6, 9 cm), as well as influent 2,4-D concentration (50, 100, 150, 300 mg $L^{-1}$) on the adsorption mechanism were investigated in their studies. This research finding confirmed that the rice husk is a cheap and sustainable bio-adsorbent, can be utilized for remediation of herbicides. As a result, RHA, for example a simple and cost-effective material, is often a suitable alternative to other carbon materials, i.e. granular activated carbon and multi-walled carbon nanotubes, etc. for remediation and diagnosis scenarios, especially in developing countries. However, it is not economically feasible to control large quantities of water.

#### 13.4.3.3 Adsorption of Pharmaceuticals

Pharmaceutical toxins have been found in groundwater sources, surface water sources such as rivers (lakes and streams), sea water, industrial discharges (influents and effluents), topsoil, and sludges. Many procedures adopted for removal of pharmaceuticals from contaminated water systems include oxidation, UV degradation as well as nanofiltration, reverse osmosis, photolysis and adsorption (Patel et al. 2019). Adsorption techniques are a low-cost approach that can be easily implemented in developing nations in which technological improvements, specialized workers and available capital are scarce, and adsorption makes it appear to become the most widely viable pharmaceutical removal method. Rice husk ash (RHA) has a natural ability to be a suitable alternative technique for the detection of pharmaceutical contaminants from industrial solvent as an agro-waste. Chen et al. (2016) discovered that RHA was an excellent bio-adsorbent for the removal of tetracycline from aqueous solution. They revealed that there are no other adsorbents that have an adsorption capacity of 8.37 mg/g, indicating that RHA is a viable adsorbent. According to them, the Langmuir adsorption isotherm is the first and most accurate in representing adsorption behaviour.

Low-cost rice husk-based activated carbon, via chemical activation method, is found to be the potential candidate for the removal of paracetamol from industrial liquid phase (Nche et al. 2017). According to the Langmuir isotherm model, the equilibrium was reached, and the volumes adsorbed were 20.964 mg/g in their research work. An increase in original paracetamol concentration as well as the duration of contact in between adsorbent and the solution resulted in an increase in paracetamol adsorption amount. Swarnalakshmi et al. (2018) proved ‘RH’ to be an effective bio-adsorbent for the removal of pharmaceuticals. HPLC technique was carried out to measure the concentration of pharmaceuticals and adsorption property. They have concluded that rice husk ash is better adsorbent than $TiO_2$ catalyst for removal the pharmaceutical contaminants. Through the use of rice husk ash produced by rice husk, a new biosorbent with a focus on affordability, safety issues and recyclable characteristics is successfully synthesized. Another promising characteristic of rice husk ash that encourages its practical use is its high efficiency with a wide pH range, along with its high stability and ease of recyclability.

Removal of two drug components, namely clofibric acid (CA) and carbamazepine (CBZ) was achieved with rice straw (Larsson et al. 2007). Their adsorption kinetics was found to follow pseudo-second-order kinetic model. Surface charge of adsorbent governs the adsorption pattern with adsorption capacities of 126.3 and 40.0 mg/g for CA and CBZ, respectively.

Despite multiple publications in this field, few are known about their individual and integrated acute and chronic exposure on plants and animals. Pharmaceutically active compounds have no worldwide specific threshold environmental concentration levels. Pharmaceutical removal is mostly done in the lab or in small-scale adoption studies. After use, bio-adsorbents is used as a biofertilizer or recycled for their thermal efficiency while also destroying adsorbed pharmaceuticals. Large-scale industrial applications have yet to be implemented. Pharmaceuticals have been removed from aqueous solutions using a bio-absorbent, i.e. rice husk ash, which have been reported in the previous research studies. This topic is a rapidly expanding and dynamic research area. Each year, new pharmaceuticals are launched in the market, necessitating an understanding of their ecological consequences and remediation.

#### 13.4.3.4 Adsorption of Fertilizers

Organic fertilizer treatments (cow or pig manure, compost, or green manure) have been shown to increase both soil adsorption and persistence of insecticides, suggesting that the organic material has a pathway for controlled release of insecticide into soil. Fluoride concentrations in drinking water that exceed acceptable levels have faced a serious threat to human health. Fluorosis is caused by fluoride levels in groundwater that exceed the WHO limit of 1.5 mg/L. Rice husk-derived nanomaterial acts as a promising candidate for removing $F^-$ from contaminated groundwater sources with enhanced ability (Goswami and Kumar 2018). The application of rice husk-derived Fe-coated active carbon-silica carbonized composite for fluoride removal from artificial waste water was found very effective (Majumdar et al. 2008). The adsorption mechanism was found effective with municipal waste water in the context of reducing fluoride concentration. Research findings by Ganvir and Das (2011), shows that rice husk ash modified with aluminium hydroxide can remove fluoride effectively from waste water. The above study revealed excellent fluoride removal rate, with enhanced adsorption capacity by modified RH.

Different forms of water bodies are mostly contaminated with phosphate, which is an ingredient of large amounts fertilizers and disinfectants. Phosphate surplus promotes uncontrolled marine plant as well as microbe growth while depleting water's reserve of dissolved oxygen. Rice husk-based activated charcoal via steam oxidation process which is used for phosphate adsorption from contaminated water gives better results compared to other activated charcoal. Mor et al. (2016) investigated the use of agro-waste rice husk ash to remove phosphate from waste water. At pH 6, a 2 g/L dose removed up to 89 percent of the phosphate in 120 minutes of contact time.

It was studied and concluded by 'Suzaimi' that rice husk porous silica grafted with branched polyethyleneimine improved the selective adsorption of phosphate as fertilizer and in households as detergent and their adsorption properties were studied via isothermal Langmuir adsorption. Figure 13.3 demonstrates the scheme showing possible adsorption mechanism of phosphate ions and pore surface diffusion mechanism onto rice husk porous silica (RSi-bPEI) in aqueous solution. The above studies suggest that these types of wastes from rice milling industries act as an inexpensive biosorbent for industrial waste water management. Agro-waste rice husk absorbent could also be used to solve its environmental hazard.

### *13.4.4 Adsorption of Phenol and Its Derivatives*

Phenolic compounds become very detrimental to health at relatively low concentration because of its toxicity and cancerous properties (Aghav et al. 2011). Phenol can be found in surface water from organic pollutants which include coal tar, oil refineries, petrochemical, gasoline, leather, plastic, rubber-proofing, paint, coking, domestic waste water, pharmaceutical, chemical spills, and steel industries (Kumar et al. 2011). Aromatic compounds, particularly phenol and its derivatives also including resorcinol, ortho-chloro phenol, nitrophenols, 2,4-Dichloro phenol, catechol, and cresols are frequently detected mostly in liquid waste among several industries (Kumar et al. 2011; Singh et al. 2008). The World Health Organization (WHO) recommends a maximum phenolic concentration of 0.001 mg/L in portable drinking water for human consumption. Prior to discharge or reuse, phenols must be reduced or eliminated. As a result, many researchers have highlighted the removal of phenol and its derivatives. A prior literature by Mbui et al. (2002) found that the adsorption of phenolic compounds by rice husk ash (RHA) adopts both the Langmuir and Freundlich models. Furthermore, they had also revealed that as the ratio of RHA weight to phenolic compound concentrations is high, so does their removal percentage from water. Thakur et al. (2017) discovered that phenolic derivative adsorption is influenced by solubility, polarization and hydroxyl group position in their research work.

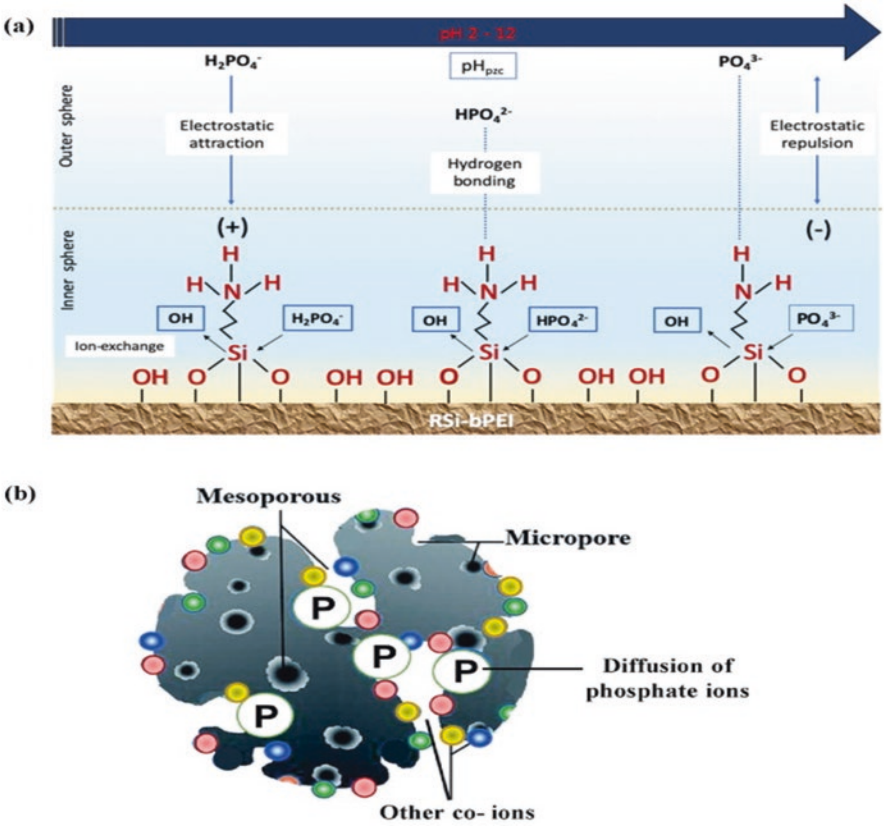

**Fig. 13.3** Scheme showing (**a**) possible adsorption mechanism of phosphate ions and (**b**) pore surface diffusion mechanism onto rice husk porous silica (RSi-bPEI) in aqueous solution (Source: Suzaimi et al. 2020)

Rice husk has the potential being used as an adsorbent to remove phenol and their derivatives because it's favourable surface characteristics as an adsorbent (Srivastava et al. 1996). Amorphous silica which is the major constituent of RH is consisted of $SiO_4.4H_2O$. Polar phenolic compounds present in waste water are removed effectively by electronegative silica framework (Si-O) of 'RHA'. (Kumar et al. 2007). Moreover, rice husk ash is much more efficient than rice husk in eliminating phenol from waste waters as equilibration times for phenol adsorption onto 'RH' itself and ash are nearly six and three hours, individually (Mahvi et al. 2004). Due to the obvious substantial quantity of phenol connected towards the adsorbent within about 120 minutes of sorption process, the adsorption kinetics is being considered super-fast.

Table 13.3 illustrates the adsorption characteristics of different phenols (mostly) as well as other organic pollutants upon 'RHA'.

**Table 13.3** Removal capacity of different phenols and their derivatives onto the RHA

| Adsorbents | Phenol and phenol derivatives | Adsorption capacity (mg/g) | Reference |
|---|---|---|---|
| Rice husk | Phenol | 4.508 | Ahmaruzzaman and Sharma (2005) |
| Rice husk | Phenol | 0.0022 | Mahvi et al. (2004) |
| Rice husk | p-chlorophenol | 14.36 | Ahmaruzzaman and Sharma (2005) |
| Rice husk | p-nitrophenol | 15.31 | Ahmaruzzaman and Sharma (2005) |
| Methacrylic acid modified rice husk | Paraquat | 317.7 | Hsu and Pan (2007) |
| Rice husk char | Phenol | 7.91 | Ahmaruzzaman and Sharma (2005) |
| Rice husk char | p-chlorophenol | 36.23 | Ahmaruzzaman and Sharma (2005) |
| Rice husk char | p-nitrophenol | 39.21 | Ahmaruzzaman and Sharma (2005) |
| Rice husk ash | Phenol | $143.99 \times 10^{-4}$ | Mbui et al. (2002) |
| Rice husk ash | Phenol | 0.886 | Mahvi et al. 2004 |
| Rice husk ash | Phenol (RHA, 300 °C) | 0.951 | Kermani et al. (2006a, 2006b) |
| Rice husk ash | Phenol (RHA, 400 °C) | 1 | Kermani et al. (2006a, 2006b) |
| Rice husk ash | Phenol (RHA, 500 °C) | 0.989 | Kermani et al. (2006a, 2006b) |
| Rice husk ash | Resorcinol | $888.59 \times 10^{-5}$ | Mbui et al. (2002) |
| Rice husk ash | 2-chlorophenol | $209.55 \times 10^{-6}$ | Mbui et al. (2002) |
| Rice husk ash | Pyridine | 11.72 | Lataye et al. (2008) |
| Rice husk ash | α-Picoline | 15.46 | Lataye et al. (2008) |
| Rice husk ash | Humic acid | 2.7 | Imyim and Prapalimrungsi (2010) |
| Activated rice husk ash | Phenol | 27.58 | Kalderis et al. (2008) |
| RHA-$NH_2$ | Humic acid | 8.2 | Imyim and Prapalimrungsi (2010) |

Rice husk and their ash were found highly effective in eliminating phenols from polluted water. Rice husk ash collected from a Kenya rice mill was utilized as a low-cost and effective biosorbents for the removal of phenolic contaminants in water (Mbui et al. 2002). RHA had a suitable phenolic compound adsorption capacity and following both the Langmuir and Freundlich isotherm models. When particularly in comparison to rice husk, RHA will necessitate less residence time to completely remove phenol. The Langmuir isotherm largely defined the adsorption mechanism behind the prepared adsorbent. The results of the column system demonstrated the feasibility about using the biosorbent obtained from RHA in water purification. After chemical and thermal treatment, RH adsorption capacity was found to increase. Increase in adsorption capacity is dependent upon treatment technique and conditions, which varies from scholar to scholar. Utilizing simple methodologies, future research will also focus on the recovery and discarding of utilized 'RH' based adsorbents.

## 13.5 Conclusions and Future Prospects

The removal of various pollutants from waste water by adsorption process with low-cost adsorbents like rice husk (RH) and rice husk ash (RHA) has been discussed in this chapter. Correlating operating constraints with adsorbent characteristics helps in the optimization of different adsorption parameters. Overall the application of 'RH' as a potential low-cost adsorbent material for waste water purification is vast. The amorphous silica in RHA makes it an efficient biosorbent. Modification of RH by both physical and chemical processes helps in enhancing its adsorption capacity subjected to the method and conditions of treatment. However, designing of adsorption experiments with modified rice husk needs further subject understanding. Application of RH based adsorbents can provide two-fold solutions, namely (1) Huge amount of RH can be transformed to value-added adsorbents, and (2) Overall the purification of waste waters using low-cost adsorbents will be a cost-effective process. For envisaging and choosing adsorbents in the submission of real waste water handling, understanding of the quantificational relationships between different adsorption parameters will provide valuable information. It is well known that during waste water treatment, because of the simultaneous presence of various pollutants, the interaction among them will obviously affect their adsorption efficiencies. Hence as a future research scope, multi-component adsorption study or more specifically competitive or co-operative adsorption study need to be performed (Sarma and Mahiuddin 2017). Most of the studies utilizing RH were of laboratory scale which need to be extrapolated to industrial experimentation for verifying the feasibility at an industrial scale. Low-cost adsorbents with great adsorption ability and simple separating efficiency are promising materials in this field of research. Additionally, development of simple methods/techniques for renewal of consumed rice husk and discarding of pollutants-bearing RH should be a future research objective.

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# Chapter 14
# Nanomaterial Composite Based Nanofiber Membrane: Synthesis to Functionalization for Wastewater Purification

**Saleem Khan, Vaishali Misra, Ajay Singh, and Vishal Singh**

**Abstract** Water has been essential element for survival and development of the living being. Our blue planet comprises 70% of the water, out of which 97.5% is saline water, and only 2.5% is freshwater. Out of freshwater 68% is permanent snow and glaciers and 30% is groundwater and 0.3% of groundwater is easily accessible for human use. With the rapid growth in global population, urbanization, and industrial development, freshwater demand has increased sharply. Also, World Health Organization (WHO) has currently reported 1.7 million deaths due to polluted water and 4 billion per year cases of waterborne diseases. These factors prompt researchers to protect existing water resource and develop new water resources through new technological development for wastewater purification. Among the currently developing water purification technology, nanomaterial-based methods are most promising due to their ability to remove organic and inorganic contaminants because of their unique properties such as size, high surface to volume area ratio, high mobility, porosity, dispensability, strong mechanical property, etc.

Nanofiber membrane-based pollutant separation technique is efficient, stable, and rapidly advancing. It has a smaller carbon footprint and performs reliable and selective separations. The membrane-based treatment process can operate at room temperature with low energy consumption. Nanofiber membrane exhibits high wastewater purification performance. To improve the performance of nanofiber membrane, inorganic, organic, and inorganic-organic hybrid nanomaterials with functionalization species can be used in the synthesis process. Modification in

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membrane materials is currently explored extensively to remove different pollutants at once by a single membrane. This chapter focuses on nanomaterial water treatment methodologies, synthesis strategies of nanofiber membrane, characterizations, and ultrafiltration demonstration in wastewater purification.

**Keywords** Wastewater · Remediation · Water purification · Nanofiber · Ultrafiltration

## 14.1 Introduction

The five elements water, air, earth, fire, and space described in *Vedas* for creation of life, among these elements, water is most essential for life and also the fundamental building block of the universe (Mohanty 1993). Water highly impacts the behavior, emotions, and health of living beings. Also, living organisms comprise high percentage of water which performs many critical functions. Thus an adequate amount of water is necessary for the smooth functioning of living bodies. Our earth has an abundance of water as a natural resource, but unfortunately, only 1% of this resource is available for human consumption (Grey et al. 2013). With the growing population and modern industries, more than 1 billion people are being deprived of clean water. It is estimated in United Nations (UN) world water development report (WWDR) (World Water Development Report *2018* | *UN-Water* 2018) that within the next 30 years water demand will increase exponentially, particularly in developing nations. Water crisis may erupt with increasing demand and reduction in availability, as depicted in Fig. 14.1.

The spontaneous rapid demand for freshwater and shrinking availability will eventually first impact locally than globally. The adulteration of freshwater by organic and inorganic contaminants will increase water scarcity at much higher rate (Schwarzenbach et al. 2006). Also, water pollution by organic and inorganic compounds increases the water scarcity factor. This concern can be overcome by protecting the existing water resources and developing new water sources. New advanced technologies for wastewater purification can help in achieving the rising demand for consumable water (Ferroudj et al. 2013). Since traditional purification methods cannot cope up with emerging contaminations to provide high purity water (Qu et al. 2013). This can be accomplished by either developing entirely new technology or enhancing current technologies with specific strategies. Among the new emerging technologies, advanced nanoscience approach has immense potential for water remediation.

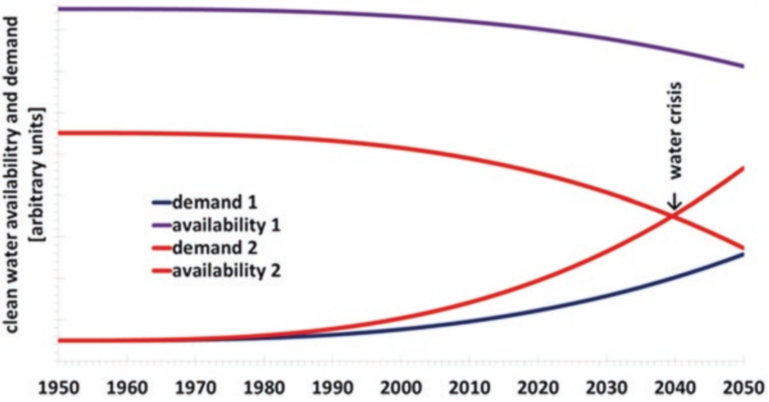

**Fig. 14.1** Projection of water availability and demand as per WWDR. Reprinted with permission from Boretti and Rosa (2019). Copyright (2019) NPJ Clean Water

### *14.1.1 Sources and Composition of Wastewater*

Wastewater is naturally generated from human activities. Water pollution or wastewater results from industrial waste, hospital waste, agricultural waste, and domestic waste. The pollutants contributed from these sectors can be characterized based on physical appearance, chemical composition, and microorganisms shown in Fig. 14.2. Various manufacturing industries release wastewater and pollutants such as heavy metals, hydrocarbons, phenols, naturally occurring radioactive material (NORM), slag, venturi sludge, organic solvents, etc. Apart from organic and inorganic waste, liquid wastewater in major quantity is produced from domestic applications (Aboelfetoh et al. 2021). Hospital produces solid, pathological, and infectious waste, whereas agricultural activities produce liquid waste comprising pesticides and insecticides. All these sectors are major contributors of water contamination. Wastewater composed of 99.9% of $H_2O$ molecules and 0.1% suspended particulates such as biodegradable organic compounds, inorganic solids, heavy metals, microorganisms, etc. (Ahmadi et al. 2020; Sher et al. 2020).

## 14.2 Nanomaterial Based Purification Methodologies

Researchers are exploring new technologies for past one decade to purify water at low cost possible. Nanoscience and materials is the emerging advance field with potential to provide high purity water at low cost with high pollutant removing efficiency and reusability. Nanomaterials exceptional properties such as size, high surface area, conductivity, mobility, mechanical strength, porosity, and more make them better option for water remediation process. Nanomaterials based advanced technologies such as nanosorbents, nanomotors, nanophotocatalysts, and

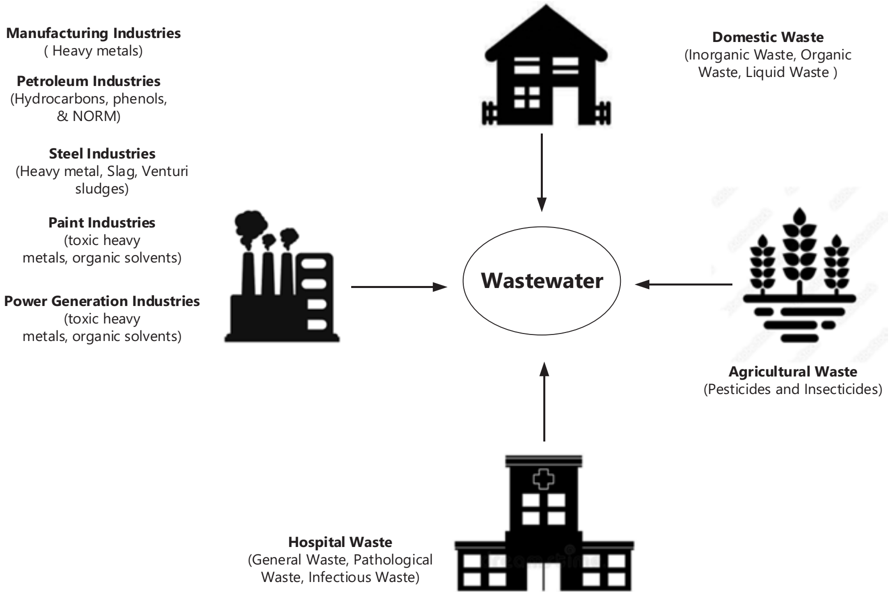

**Fig. 14.2** Wastewater sources from urban and rural area

nanomembrane are positive prospects for water purification (Bora and Dutta 2014; Kalfa et al. 2020).

### *14.2.1 Nanophotocatalysts*

The interaction of nanomaterial and light energy is of significantly important because of their broad and effective photocatalytic activities for numerous pollutants (Dutta et al. 2014; Kurian and Nair 2016). The term photocatalysis is a combination of two Greek words "photo" and "catalysis" which means compounds decomposition under light. It is also known as the process by which substance is activated by light. Water purification is commonly carried out with the help of nanophotocatalysts as they improve catalyst reactivity because of higher surface area (Adeleye et al. 2016). Nanocatalysts produce oxidizing species at the surface making the oxidation process faster which degrades the pollutant effectively. The photocatalysis can be distributed into five steps as follows:

1. Diffusion reaction at surface of photocatalyst
2. Adsorption at the surface of photocatalyst
3. Reaction of adsorbed particulates
4. Desorption from the surface
5. Removal of reactant products

Homogenous and heterogeneous photocatalyst are classified based on the chemical process used in photocatalytics. A homogenous photocatalytic system exists when the reactants and photocatalysts are in same phase. These photocatalyst systems are developed to generate highly reactive species of OH radicals which are specifically designed for the removal of water pollutants like photon/fenton, ozone/ultraviolet (UV), and $H_2O_2$/UV system (Nakamura et al. 1995; Murthy et al. 2017). These are advanced oxidation processes where $H_2O_2$ and ozone oxidants interact with UV sources to release hydroxyl (OH) radicals, which oxidizes dissolved pollutants in water. Fenton oxidants-based systems are responsible for eliminating undissolved contaminants in the water, where ferrous salt and $H_2O_2$ produce the required OH radicals. Homogenous photocatalyst systems are mostly synthesized using transition metals, since the product possesses metal ligand for coordination with other molecules for water remediation.

In heterogeneous photocatalyst system, the reactant molecules and photocatalysts are in different phase. Generally, this system comprises of dispersed semiconductor material in liquid or gas phase. The photocatalysis reaction occurs on the surface of the material. This is a polyphasic process in which different phases materials are working in coordination. In heterogeneous photocatalyst system, semiconductor materials have solid phase and liquid reactant has fluid phase. Photons activate the solid phase materials or substrates to produce charges to stimulate reactions. Photon flux is also known as electromagnetic phase. Semiconductor material exhibits energy bandgap between valence and conductance band. Thus when surface interacts with photon having higher energy than bandgap, electron shifts from valance to conduction band. The migration of electron from the surface reduces molecules, the adsorbed molecules on the surface of material oxidizes by positive charge. Bandgap of the materials controls the charge transfer rate to the adsorbed molecules. Simultaneously volume recombination or surface recombination also occurs causing heat dissipation, hence heterogeneous photocatalysis process is exothermic (Kibria et al. 2015; Ebaid et al. 2017). Nanophotocatalyst is a low temperature vital process for removal of organic contaminants for water. Also, nanophotocatalyst materials have properties such as nontoxic, cost effective, availability, and photoactive. Nanophotocatalyst comprising of nano sized semiconductor metals is used to degrade organic contaminants like pesticides, volatile organic compounds, detergents, and dyes. Also it can be used for removal of heavy metals, halogenated, and non-halogenated compounds (Gómez-Pastora et al. 2017). Table 14.1 summarizes efficiency of photocatalysts water contaminants removal.

### *14.2.2 Nanosorbents*

Nanosorbents have unique sorption feature which makes them suitable and robust method for water purification. Researchers are exploring new methods to produce nanosorbents in large quantity for commercial purpose. The physical, chemical, and material properties are important for nanosorbents to innate surfaces and

**Table 14.1** Nanophotocatalysts contaminants removal efficiency

| Nanophotocatalysts material | Contaminant removed | Removal efficiency | Reference |
|---|---|---|---|
| $Ti_2CO$ | Methylene blue | 10 μmol/L | (Guan et al. 2016) |
| $TiO_2$/trititanate | Rhodamine B | >91% | (Chen et al. 2015) |
| AgBr/ZnO | Methylene blue | 87% | (Dai et al. 2014) |
| 3D SnO | Methyl orange | 83% | (Cui et al. 2015) |
| ZnO nanorods | Rhodamine B | – | (Fang et al. 2015) |
| Zero-valent nanocopper | Methyl orange | 35% | (Liu et al. 2016) |
| $TiO_2$ | Methyl orange | 30% | (Wang et al. 2016) |
| $CuFe_2O_4@C_3N_4$ | Orange II | 98% | (Yao et al. 2015) |
| $Ag_3PO_4/BiPO_4/Cu$ (tpa). grapheme | Atrazine herbicide | 80% | (Mohaghegh et al. 2015) |
| Carbon nanorods $TiO_2$ | 2,4-dichlorophenol | 96% | (Ortega-Liebana et al. 2016) |

functionalization (Khajeh et al. 2013). Nanosorbents based on their adsorption process can be categorized into various groups such as metal nanoparticles, oxide nanoparticles, carbon nanotubes, nanosheets, and carbon nanoparticles. Parameters like size, surface chemistry, composition, crystal structure, agglomeration, and solubility control the properties of nanosorbents (Kalfa et al. 2009). Nanoparticles with fine grain size are chemically active which is prominent property for nanosorbent. Inorganic metal and non-metal oxide nanoparticles based nanosorbents are used for removal of hazardous contaminants from wastewater. Polymer-based nanosorbents provide sustainability to environment and effective wastewater remediation (Pandey et al. 2017). Commonly used polymers with cost effective feature for nanosorbents are nanomagnetic polymer, covalent, extracellular polymers, etc. (Alaba et al. 2018). Cellulose-driven polymers are nontoxic and excellent adsorbents.

Carbon-based nanomaterials are extensively studied for wastewater purification due to their extraordinary efficiency to eradicate heavy metals and organic pollutants. Activated carbon is the most common nanosorbent used because of high porosity and high surface area (Ren et al. 2011). Single wall carbon nanotube (SWCNT) and multiwall carbon nanotube (MWCNT) are being prepared using graphene sheets for adsorbents synthesis. The hollow structures of CNTs can provide tunable attribute to the nanosorbents. Nanosorbents efficiency to remove heavy metals from wastewater is highly influenced by factors such as temperature, pH, concentration of adsorbent, and contact time. Researchers have reported that maximum Zn metal contamination is removed from water with nanosorbent pH value of 5.5. When the pH level is increased, the adsorption efficiency was reduced (Srivastava et al. 2015). Adsorption phenomenon increases with higher contact time. The adsorption of heavy metal is high in initial stage and as the contact time increases, active sites are blocked contaminants. Nanoparticles are being explored as nanosorbents because of their size, chemical activity, and adsorption capability. Also nanoparticles have the capability to remove heavy metals, high adsorption parameter, and ability to adsorb concentration up to ppb. Carbon nanoparticles such as carbon black, graphene, and

**Table 14.2** Nanosorbents heavy metal removal efficiency

| Nanosorbent material | Contaminant removed | Removal efficiency | Reference |
|---|---|---|---|
| Magnetic MWCNTs | Cr(VI) | 100 | (Huang 2015) |
| Magnetic zeolite-polymer composite | V | 73 | (Mthombeni et al. 2015) |
| ZIF-8 nanoparticles | As | 60.03 | (Jian et al. 2015) |
| ZnS nanocrystals | Hg (II) | 99.99 | (Qu et al. 2014) |
| Decorated magnetite | $Cu^{2+}$ | 99 | (Neyaz and Siddiqui 2015) |
| Graphene nanosheets (GNS)/δ-$MnO_2$ | Ni (II) | 77.04 | (Varma et al. 2013) |
| Nanocrystalline titanium dioxide | As (III) | >98 | (Maria Pena et al. 2006) |
| Magnetic nanoparticles coated zeolite | As (III) | 95.6 | (Salem Attia et al. 2013) |
| Magnetic nano-adsorbent | $Pb^{2+}$ | 80 | (Khani et al. 2016) |
| PMDA/TMSPEDA | Zn (II) | 95 | (Alsohaimi et al. 2015) |

graphene oxide, metal nanoparticles, metal oxide nanoparticles, and polymer-based nanosorbents are reported for water purification. Also nanomaterial composites of various materials are highly used in the water remediation process (Gusain et al. 2020). Table 14.2 summarizes the efficiency of nanosorbents for heavy metal removal from water.

### *14.2.3 Nanomembranes*

Nanomembrane is outstanding and most effective technology for water purification. These membranes are enabled by new functionalities like reactivity, permeability, and fouling resistance. Also this technology is highly economical, effective, simple design and requires less space (Nair et al. 2012). Nanomembranes are fabricated using one dimensional organic and inorganic nanomaterials such as nanofibers, nanoribbons, and nanotubes. These membranes can eliminate nanoparticles present in the water at very high speed. Various multifunctional membranes are reported mixing different nanomaterials on polymer membrane. Phenomena like nanofiltration (NF), ultrafiltration (UF), reverse osmosis (RO), etc. are performed using nanomembrane having porous substrate with nanomaterial composite layer. These membranes are used to effectively remove dyes and heavy metals (Bowen and Mukhtar 1996; Han et al. 2013; Mulyanti and Susanto 2018). Fouling of hydrophobic membrane is caused by its interaction with organic contaminants. Also the deposition of nanoparticles on outer surface and within the pores of membrane increases the membrane fouling (Yang et al. 2015). This effects the water purification efficiency and reliability of the filtration system. Various techniques such as membrane

**Table 14.3** Nanomembrane contaminant removal efficiency

| Nanomembrane material | Contaminant removed | Removal efficiency | Reference |
|---|---|---|---|
| PVDF | NaCl | <280 ppm | (Feng et al. 2008) |
| Aquaporin reconstituted | $MgCl_2$ | 88.1% | (Sun et al. 2013) |
| Zr-MOF | $Al^{3+}$ | 99.3% | (Liu et al. 2015) |
| CNT-PcH | NaCL | 99.99% | (Tijing et al. 2016) |
| MCM41-PA-TFN | $Na_2SO_4$ | 97.3% | (Yin et al. 2012) |
| GO-PA-TFN | $Mg^{2+}$, $Ca^{2+}$, $Na^+$ | ~100% | (Yin et al. 2016) |
| $K^+$-controlled GO | Metal cations and dye cations | ≥6 Å | (Chen et al. 2017) |
| Single-layer graphene | Salt cations, methylene blue, rhodamine-WT | 93–95% | (Surwade et al. 2015) |
| $Ti_3C_2T_x$ Mxene | $Na_2SO_4$ | 56.7% | (Ren et al. 2015) |
| GO | $Cu^{2+}$, $Na^+$, orange 7 | ~100% | (Hu and Mi 2013) |

modification, operation conditions, and replacing feed solution are used to minimize the membrane fouling problem (Su et al. 2011). Table 14.3 summarizes the nanomembrane contaminants removal efficiency.

Nanofibers high aspect ratio gives them unique interlocking property to form freestanding porous membrane. Cellulose fibers based membranes are the oldest membrane which are chemically and thermally stable. New methods are being developed for the synthesis of cellulose-based nanofiber membrane for air and liquid purification because of its mechanical strength, film development, surface enhancement, and safety (Isogai et al. 2011). Nanofiber as fillers in thin-film nanocomposite (TFN) is fabricated by interfacial polymerization. Also CNTs are sulfonated to integrated with TFN (Zheng et al. 2017). The nanofiber membrane has an advantage over traditional membrane as they don't require ion exchangers for water purification process.

## 14.3 Fabrication of Nanofiber Membrane

Nanomembrane for water remediation can be fabricated using organic, inorganic, and hybrid nanomaterials (Li et al. 2013). Various fabrication techniques like phase inversion, track etching, interfacial polymerization, and electrospinning are used for this purpose (Jackson and Hillmyer 2010; Ahmed et al. 2015). In phase inversion method, a controlled method is used to convert homogenous solution into solid. Various transformation methods such as precipitate immersion, thermo, vapor, and evaporation phase separation are used for conversion process. In order to fabricate NF, UF, and RO membrane immersion and thermo induced methods are widely used (Khorshidi et al. 2016). Interfacial polymerization is process of polycondensation reaction of two monomers used to fabricate NF and RO membrane. The structure of the membrane can be controlled by factors such as monomers concentration, time, solvent, and posttreatment (Sadrzadeh and Bhattacharjee 2013). Track etch process is the irradiation of non-porous polymer with high energy ions to create nanopores in membrane (Wang et al. 2017).

Electrospinning technique to fabricate nanofiber-based membrane has been developed two decades ago and it's been improving ever since (Sun et al. 2014). In this method of fabrication, polymer solution is melted using high voltage which controls the morphology of the fibers (Zhang et al. 2013). Conventional electrospinning system consists of high voltage source, thruster, syringe, and metal collector. In the fabrication process, thruster injects the solution into electric field (Arribas et al. 2019). The high voltage field charges the rotating solution and generates the force to overcome the surface tension. The shape of droplet is converted into Taylor cone which form the jet and the ejected jet from syringe causes the unstable bending (Collins et al. 2007). The accelerated jet is received at the low potential and when the solvent is evaporated the polymer chain prevents the breakage, hence nanofiber is deposited over the substrate (Huang et al. 2019). Figure 14.3 shows the various membrane based on nanoparticles, CNT, nanosheets, and nanofibers (Ying et al. 2017).

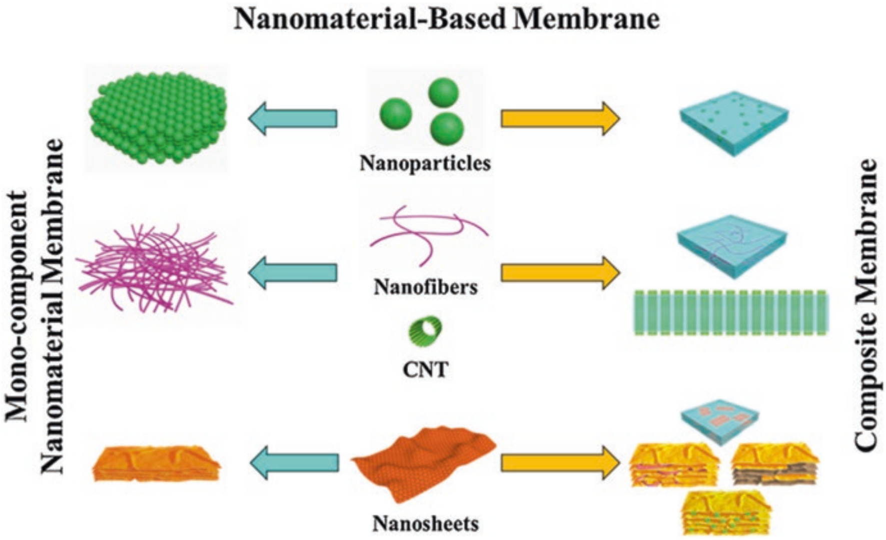

**Fig. 14.3** Nanomaterial-based membrane for water remediation. Reprinted with permission from Ying et al. (2017). Copyright (2017) Applied Materials Today

### *14.3.1 Functionalization of Nanofiber Membrane*

Functionalized nanofiber membranes are required to perform complex wastewater purification process. New methods are being developed to functionalize electrospun nanofiber. Various functional materials are blended with nanofiber using preelectrospinning and postelectrospinning process (Cui et al. 2020). The most common method to acquire functional nanofiber membrane is to modify it with nanoparticles, polymer addition, and coaxial spinning (Mishra et al. 2018). The diameter of nanofibers directly influences the flux level, and their toughness affects the mechanical strength. The quality of electrospun nanofibers has a substantial impact on ENMs performance. In order to achieve stable functionalized nanofiber membrane researchers dope solution material with carbon, metal, and inorganic nanomaterials. These functionalized nanofiber membranes are used in medicines, food, and especially in wastewater treatment (Akther et al. 2019). CNTs are integrated with polymer nanofiber because of tensile and strength property (Ajayan et al. 1994). Since graphene oxide (GO) and reduced graphene oxide (rGO) are excellent nanomaterial in water purification because of their excellent properties of adsorption, photocatalysis, and antibacterial (Sundaran et al. 2019). Also integrating GO nanosheet with electrospun nanofiber membrane of PVDF, it is reported that 99.9% of salt rejection is obtained in water distillation process (Li et al. 2020). Since the modification of nanofiber surface is very complicated, thus membrane surface modification/functionalization processes are adopted. The surface of the membrane is modified using various deposition process (Suwaileh et al. 2018). Zhang and team achieved purification of oily water using polyimide nanofiber membrane deposited with polydimethylsiloxane (PDMS) and zinc oxide (ZnO) (Zhang et al. 2020). Since the smallest pore of nanofiber ranges up to several hundred nanometers, it is impossible to trap smaller size particles in membrane. Thus modification of electrospun nanofiber membrane is carried out using crosslinking polymerization process. The filtration membrane consists of supporting nanofiber layer and active thin-film nanofiber composite. Chemically altering the electrospun nanofiber membrane is viable option to functionalization of the membrane for high water purification efficiency. Physical grafting of nanofiber membrane using layer by layer (LBL) and plasma method based attachment of functional groups like nanoparticles, polyelectrolytes, and metal oxide are reliable process but stability is still a challenge due to long-term operation of water purification process. Chemical grafting of nanofiber membrane can overcome the stability factor effectively. The functional groups are attached to nanofiber membrane by chemical reaction. Because of high specific area of functional groups, absorption capacity of the electrospun nanofiber membrane increases manifolds (Xu et al. 2017). Strong bacterial inactivation under visible light spectrum is achieved by co-spinning of methylene blue (MB) functionalized group with PMMA/methacrylic acid nanofibers (Wang et al. 2018). Also GO grafted with nanofiber of dopamine methacrylamide shows substantial antimicrobial activity against both Gram positive and negative bacteria (Zhang et al. 2018). Chemical alternation of electrospun nanofiber membrane with functionalized groups is playing important role.

#### 14.3.1.1 Nanofiber Functionalization Methods

Nanofiber membrane has high surface to volume ratio which is highly beneficial to immobilize nanoparticle and biological molecules flowing through it. Electrospinning method has the benefit of allowing the synthesis of continuous polymer fibers with diameters ranging from hundreds nanometers to micrometers. Electrospinning can be used to create 3D interconnected nanofibers doped with metal, metal oxide, and ceramic nanoparticles. Also implanting various functional molecules onto electrospun nanofibers can improve surface qualities such as wettability and roughness.

##### Polymer Surface Activation

Immobilization of contamination in water passing through nanofiber membrane is possible by implanting various functionalization materials on electrospun nanofiber. To activate the polymer, various approaches which include chemical treatment, surface oxidation, and plasma treatment are suitable.

- Plasma treatment: It's a useful method that uses the nature of plasma to deliver a variety of functional groups to the polymer surface. Plasma is created by energizing gases with microwaves, radiofrequency, and electrons from a hot filament discharge. The energized particles form reactive radicals by breaking polymers molecular bond. Depending on the composition of plasma, polar functional moieties like carbonyl (>C=O), carboxyl (–COOH), hydroxyl (–OH), hydroperoxides (HOO–), and amines (–$NH_2$) are incorporated with electrospun polymer. These functional groups enhance electrostatic interaction. Improvement in surface cell attachment to hydrophobic polymer enhances by adding functional group.
- Chemical surface degradation treatment: In this method hydrolysis or aminolysis process is carried out to partial degrade polymer surfaces. Elimination of etching chemicals after the process is required, whereas plasma treatment by-products are volatile, resulting in less material degradation than acid etching. The subsequent processes must be carried out carefully because failure to do so will result in the complete disintegration of electrospun fibers.

##### Covalent Bonding

Nucleophiles such as hydroxyl (–OH), amines (–$NH_2$), alkoxides, carboxylate, and thiols are chemical entities that contain a pair of electrons capable of forming a covalent bond when reacting with electrophiles. Electrophilic centers on the polymer surface can react with the functional groups of biomolecules to form addition or substitution reactions, making immobilization on the polymer surface easier.

- Esterification: It's the process of formation of esters by reacting organic or inorganic acid with hydroxyl group. Esterification reaction can yield functionalized nanofiber with various hydroxyl or carboxylic groups. Through this process, ethylene vinyl alcohol electrospun nanofibers functionalized with citric acid groups provide carboxylic acid groups suited for lysozyme adsorption and protein purification.

- Click chemistry: The tolerant available in aqueous environment for biomacromolecules functionalization. Click reaction has high yield of nontoxic molecules. Various functional compounds are also immobilized on electrospun nanofibers surfaces using click reactions.
- Crosslinker-assisted process: Crosslinking compounds help to immobilize a variety of functional components on polymer surfaces, including proteins, enzymes, and hydrophobic residues. They are also commonly utilized to inter- or intra-chain link polymeric nanofibers to keep them stable. The crosslinking process is also physical properties of the nanofibers.

#### Radical Polymerization Process

Radical polymerization method is to modify the surface properties like wettability, roughness, etc. of nanofibers. This method has limitation such as poor composition, molecular weight, chain linking, and polydispersity. These limitations can be overcome by using control or living radical polymerization process.

#### Noncovalent Immobilization Process

Adsorption of functional groups is used to alter the surface of the electrospun nanofibers. It’s a complicated method to control. Electrostatic interactions, hydrogen bonds, van der Waals interactions, and hydrophobic interactions are only some of the weak interactions that can occur in this process. Nanofibers can be functionalized by grafting organic molecules, metal oxide, ceramics, etc.

### *14.3.2 Factors Effecting Morphology of Nanofiber Membrane*

Electrospun nanofiber membrane morphology is greatly influenced by solution properties (concentration, viscosity, resistivity, and molecular weight), processing (flow rate, input voltage, and separation between tip and collector), and surrounding parameters (temperature and humidity) (Li and Wang 2013).

#### 14.3.2.1 Solution Parameter Effect

The electrospinning process for nanofiber synthesis significantly depends upon the concentration of the polymer solution. As the concentration of the polymer solution is decreased, the applied voltage causes polymer entanglement which form nano beads instead of nanofiber. When the solution concentration is increased beaded nanofibers are synthesized. Optimized concentration, results in proper solution viscosity and surface tension which leads to synthesis of smooth nanofibers. Increasing the concentration of polymer solution above critical concentration results in clogging phenomenon which causes formation of helix micro ribbons (Senthil and Anandhan 2013). Viscosity and molecular weight influence the morphological properties of the nanofiber. Thick nanofibers are synthesized at higher viscosity of the solution and at low viscosity polymer entanglement results which form beads or beaded fibers. At optimum viscosity of solution, viscoelastic force restricts the polymer chain fragmentation resulting in uniform continuous fibers. The diameter of the nanofibers depends upon the conductivity of the solution and it affects the formation of Tylor cone. These cones are formed only when solution is conductive. As the stable Tylor cones are formed at optimum conductivity, it will result in uniform thin nanofibers (Cramariuc et al. 2013; Mohammad Ali Zadeh et al. 2014).

#### 14.3.2.2 Processing Parameter Effect

Voltage is important in converting a solution droplet at the tip of a spinneret into a Taylor cone, which is the first step in jet formation. The range of applied voltage depends upon the solution parameters. The coulombic repulsion of charges within the jet increases as the voltage increases. As a result, the jet will stretch forming thin nanofibers. Increasing the voltage above optimum value leads to formation of beaded nanofiber or cylindrical nanofibers (Matabola and Moutloali 2013). Flow rate also influences the diameter of the nanofiber. Low flow rate causes insufficient supply of polymer solution to the spinneret, which restricts the formation of Tylor cone. Flow rate depends upon nature of the polymer solution.

#### 14.3.2.3 Ambient Parameter Effect

Ambient parameters such as temperature and humidity strongly affect the surface morphology and diameter of the nanofibers. Electrospinning process is not possible at high humidity and increasing humidity causes reduction in diameter. Humidity acts as the plasticizing agent which causes crystal instability and affects the surface and interior regions (Moutsatsou et al. 2015).

## *14.3.3 Filtration process*

Advances in electrospinning technology development of functionalization materials for nanofiber membrane have encouraged researchers to explore membrane purification processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and forward osmosis (FO).

### 14.3.3.1 Microfiltration

Microfiltration (MF) process is a prefiltration process used in various membrane filtration to separate contaminants having particle size ranging from 0.1 μm to 10 μm which includes bacteria (Hu et al. 2015). Fabrication of MF using electrospinning process provides characteristics such as controlled membrane pore size and easy manufacturing. This process also causes insufficient mechanical strength. Also the MF performance is effected by the flux and selectivity. By adjusting the spinning process parameters MF membrane performance can be improved. The pore size is influenced by the membrane porosity and fiber diameter, whereas the film thickness is nearly constant. Furthermore, they discovered that hot pressing reduces porosity and improves rejection performance.

### 14.3.3.2 Ultrafiltration

Ultrafiltration (UF) process allows passage to water molecules or particles through membrane using hydrostatic pressure. The pore size in UF membrane ranges from 0.01 to 0.1 μm. In various water remediation fields, such as drinking water, distillation, and water reusability, UF can immobilize suspended particles, colloidal, and microbiological viruses, and it is frequently employed to purify water. UF membranes made by the phase inversion approach are contentious in actual applications due to their low productivity and pollutant susceptibility. The closed big pores in the UF membrane generated by the phase inversion approach restrict the water molecules to pass during the diffusion process, highlighting the need for a porous substrate and a thin selective layer in the electrospun UF membrane (Dobosz et al. 2017).

### 14.3.3.3 Nanofiltration

Nanofiltration (NF) is a membrane technology to seize the flow of particles having size 100–1000 Da and it has been used in wastewater purification process (Labban et al. 2017). Researchers have reported removal of odor, trace organic contaminants, and ions using NF membrane (Li et al. 2015; Prykhodko et al. 2021). NF membrane can efficiently remove divalent and multivalent ions (Xu et al. 2019).

#### 14.3.3.4 Reverse Osmosis

Reverse osmosis (RO) is a membrane separation technology driven by pressure. RO membrane pore size distribution ranges from 0.1 to 1 nm (Asadollahi et al. 2017). RO membrane can block monovalent ions like $Cl^-$ and $Na^+$ which can be used for water desalination (Greenlee et al. 2009). Because of its susceptibility to microbes, the first RO membrane was composed of cellulose acetate, which limited its application.

#### 14.3.3.5 Forward Osmosis

The concentration gradient causes osmotic pressure which moves water spontaneously from low concentration to high concentration solution. The forward osmosis (FO) allows water molecules to pass through membrane and rejecting ions. FO process consumes low energy, wide range of separation, high water recovery, and effective fouling (Phuntsho et al. 2013).

## 14.4 Application of Nanofiber Membrane for Water Purification

Nanofiber membrane can be utilized to remove organic, inorganic, and biological pollutants. In this section, nanomembrane applications in contaminations removal have been discussed.

### *14.4.1 Cations*

Polymer materials have outstanding permeability, mechanical and chemical stability for nanomembrane preparation or supporting substrate for hybrid nanomembrane. Feng and team fabricated PVDF-based nanofiber membrane using electrospinning technique for water detoxification (Feng et al. 2008). The membrane produced purified water with 280 ppm NaCl concentration, when the 6% weight of NaCl is added to water. The membrane showed reusability after several days of using it.

### 14.4.2 Anions

Bolisetty and co-worker fabricated hybrid nanomembrane using β-lactoglobulin, amyloid fibrils, and activated carbon by employing vacuum filtration. The membrane removed 99% of $AsO_4^{3-}$ and $AsO_3^{3-}$ anions from water contaminated by arsenic by interaction of metal-ligand supermolecules having high reusability (Bolisetty et al. 2017).

### 14.4.3 Nanoparticles Filtration

DesOrmeaux et al. used porous silicon to fabricated silicon nitride nanoporous membrane to remove gold (Ag) nanoparticle from the water. It is reported that 40–80 nm Ag nanoparticles were removed by adjusting the mask layer in ion etching process. The fabricated membrane can remove 80% of the Ag nanoparticles from water (DesOrmeaux et al. 2014). Similarly, various researchers have reported that different nanoparticles can be removed from water using nanofiber membrane (Li et al. 2010; Bolisetty and Mezzenga 2016).

### 14.4.4 Organic Contaminants

Organic contaminants like oil, proteins, and chemicals are harmful to one's health and must be eliminated from drinkable water. When compared to physical retention, modification or functionalization of ENMs could be a potential approach for removing organic molecules from water. Due to industrial manufacture, oil is a frequent organic component found in wastewater. Oil has been removed from water using porous membranes having a hierarchical structure. The dissolved oxygen in the water is affected by pollutant such as hydrocarbons, phenols, oil, and pesticides which is life threatening for aquatic ecosystem. Protein is another organic molecule that is frequently encountered, particularly in wastewater treatment. Protein concentrations as low as 1% in the river can deplete dissolved oxygen, resulting in the extinction of aquatic life in the river. To extract the protein from water, ENMs could be functionalized with efficient moieties that have a high affinity for proteins. Textile, paper, and plastic sectors produce a substantial amount of reactive azo dye in their wastewater. These dyes can be harmful and carcinogenic to aquatic living species once they enter the environment. As a result, they are regarded as one of the most significant sources of water contamination that must be handled. Karim et al. synthesized chitosan-based nanoporous membrane using freeze drying method. The prepared membrane has low water flux; 98%, 84%, and 70% of Victoria Blue, Methyl Violet, and Rhodamine 6G respectively were removed from the water (Karim et al. 2014).

### *14.4.5 Biological Contaminants*

Algae, bacteria, planktons, and virus biological contaminants in water causes various diseases. Zhang et al. synthesized UF nanomembrane structure using $TiO_2$ nanowires having diameter of 10 nm. It is reported that nanomembrane can effectively remove polyethylene glycol (PEG) and polyethylene oxide (PEO) dissolved in the water. Also under UV irradiation PEG, PEO and other inactive biological contaminants can be destroyed (Karim et al. 2014). Table 14.4 summarizes various nanofiber membranes and their contamination removal application.

## 14.5 Barriers Associated with Nanomaterial-Based Water Purification

Nanomaterials based wastewater remediation is a promising approach but there are significant risks associated with it. The prominent barriers are toxicity, cost, and acceptability.

**Table 14.4** Summary of contaminants removed by various nanofibers with functional group

| Nanofiber | Functional group | Contaminant | Reference |
|---|---|---|---|
| Polyacrylonitrile | silica and silver nanoparticles | *E. coli* | (Mataram et al. 2015) |
| Polyacrylonitrile | ZnO or CuO NPs | *S. aureus* | (Shalaby et al. 2018) |
| Zonal silica nanofiber | Sulfhydryl | Hg(II) | (Li et al. 2011) |
| Carbon nanofiber | Carboxyl | Cu(II) | (Ahmad et al. 2020) |
| MgS/cellulose Nanofiber | Sulfinyl | Cd(II) | (Sankararamakrishnan et al. 2019) |
| Titanate nanofibers | –O–Ti | Pb(II) | (Yang et al. 2008) |
| EVOH/PPy nanofiber | Amine | Cr(VI) | (Yalcinkaya 2019) |
| CS/PGMA/PEI Nanofiber | Amine | Cr(VI), Cu(II), Co(II) | (Yang et al. 2019) |
| MgO/PPG nanofiber | Amide | Pb(II), Cu(II), Cd(II) | (Almasian et al. 2018) |
| PAN nanofiber | Carboxyl | Cu(II), Pb(II), Zn(II) | (Morillo Martín et al. 2018) |

### 14.5.1 Toxicity

The conventional wastewater purification method includes chlorination; it was presumed to enhance the life expectancy but the by-product obtained from this process includes toxic compounds like N-nitrosodimethylamine and trihalomethanes (Raza et al. 2016). Nanomaterials properties which make it useful can also result in polluting the water. Due to the small size of nanomaterials it can end up in damaging human organs (Sukhanova et al. 2018).

### 14.5.2 Cost Effectiveness

The acceptance of nanotechnology for wastewater treatment is influenced by its quality and cost. In developed countries, advanced wastewater treatment methods are used to eradicate a wide range of contaminants; however, in emerging nations, it typically only meets the most basic demands (e.g., disinfectant). In both circumstances, there is a need to treat increasingly complex pollutant mixes in order to achieve improved water quality at a cheaper cost, pushing the limits of current wastewater remediation models. As a result, while this cost barrier is important, it is not insurmountable (Qu et al. 2012).

### 14.5.3 Nanomaterial Ecotoxicity

Ecotoxicity is the dispersion of chemical, physical, or biological contaminants to disturb the ecosystem. During the synthesis process of nanomaterials, there is potential risk of leakage of nanomaterials in the ecosystem. The toxic effects of Ag NPs and $TiO_2$-NPs on the growth of duckweed were explored by researchers and reported that these developing nanomaterials represent a major concern for the aquatic environment (Kim et al. 2011).

## 14.6 Conclusion

In the prevailing time and forecasted situation about usable freshwater demand and availability, modern water remediation technologies are required to ensure good water quality by eradicating chemical and biological contaminants. Nanotechnology is among the best approach for water purification and effectiveness of using nanomaterials in wastewater treatment is undeniable. Extensive research is required to develop cost effective synthesis approach. Electrospinning of polymer is highly effective technique for nanofiber membrane fabrication and the properties of electrospun nanofiber membrane are directly determined by the operation circumstances and spinning solution parameters. Their large surface to volume area, pore interconnectivity, pore size uniformity, and simplicity of inclusion into functional nanomaterials, and deposition on porous substrate is an excellent choice for wastewater purification with minimum risk of contaminating the water itself. Nanofiber membrane functionalized with doping of nanoparticles, surface coating crosslinking or grafting, and other methods, allowing them to remove various organic and inorganic contaminations. Nanofiber membrane is a great way to improve the structure and performance of water treatment materials at the development stage.

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# Chapter 15
# Enzymes and Its Nano-scaffold for Remediation of Organic Matter in Wastewater: A Green Bioprocess

**Saumya Khare and Shikha**

**Abstract** In the past few decades, remediation and management of water resources has been a major challenge. Global increase in population and industrialization has burdened the water resources. The organic pollutants discharged in wastewater from industries and anthropogenic activities have been major driving force that causes a threat to water resources. By 2050, around 5.7 billion people are expected to have a residence in the area with water scarcity for more than a month in a year. The urge is to achieve environmental sustainability by adopting sustainable alternatives for treating and managing organic pollutants using clean and eco-friendly alternatives.

Enzymatic bioremediation is a green bioprocess that provides efficient detoxification of organic waste using myriad of enzymes. In this context, chapter gives an overview of organic pollutants present in wastewater and its impact on the environment and human health. This encompasses enzymatic bioremediation strategies to detoxify organic pollutants with an attempt to highlight the role of diverse range of enzymes, and the key challenges of enzymatic bioremediation. The emerging role of nanotechnology integrated with conventional bioprocess is amalgamated to provide sustainable, green, and energy-efficient bioremediation.

**Keywords** Organic pollutants · Wastewater · Remediation · Bioprocess

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## 15.1 Introduction

Water plays a vital role for sustaining life on the earth. Over the past couple of decades, increasing global population, industrialization, change in agricultural practices, and climatic conditions compounded with other anthropogenic human activities have caused adverse impacts on the water resources. Amplified use of water resources and their overexploitation deteriorates the water quality with change in nutrient balance, affecting the living flora and fauna, ecosystem services, aesthetic value, recreation, and human well-being. Recently, biorefineries have attracted wider interest as environmentally friendly alternatives for bioenergy and food production (Khare 2021). However, with changing climatic conditions, energy and food production anticipate to escalate the complexity of the food-energy-water nexus with rising population, socio-economic development, and water demand.

The problem of water scarcity has come up as an alarming situation with limited water availability for human consumption. Around 2.3 billion people resides under water stress countries (UN Water 2021). According to the UN SDGs report UN Water (2021), billions of people do not have access to safe drinking water, sanitation, and hygiene. This accounts for 2 billion people (26%) having a shortage of safe drinking water, 3.6 billion people (46%) lacking proper sanitation, and 2.3 billion people (29%) are deficit of basic hygiene. The aim is to ensure availability and sustainable management of water and sanitation for all (Goal6 # UN SDG n.d.). However, United Nations has declared the year 2018–2028 as decade of water for sustainable development. In this backdrop, proper management, conservation, restoration, and sustainable use of water resources are of utmost importance.

On the other hand, environmental pollutant has exacerbated the water resources. Among various pollutants, water is most vulnerable to organic pollutants. Domestic sewage and industrial effluents carrying organic pollutants directly or indirectly reach to the water bodies, causing risk to humans, animals, and aquatic organisms. Majority of organic pollutants like pharmaceutical compounds, dyes, personal care products, and estrogen disrupters are grouped as emerging pollutants. The major environmental challenge is to regulate the mismanaged release of organic pollutants and their removal from the environment by implementing efficient wastewater treatment technologies. However, most of these contaminants are recalcitrant, and hence, the urge is to opt for the promising remediation technology, which ensures public health security. Various conventional technologies viz., physico-chemical and biochemical are available, but these often lack efficient management and mitigation of organic pollutants. Nevertheless, these methods face major constraints like higher operational charges, lower efficiency, risk of generating secondary pollution (Zdarta et al. 2021), environmental toxicity, and lack of skilled manpower.

Bioremediation is a promising, eco-friendly and economical alternative, which utilizes potential of biological agents like plants, microorganisms, and biological catalyst for mitigating toxic organic/inorganic pollutants (Singh and Walker 2006; Saxena et al. 2020). In recent decades, environmental biocatalysis has attracted the attention of researchers from the worldwide to curb the problems associated with organic pollutants, the environment and their long-term impact on health issues. Enzymes are highly efficient biological catalyst operative under mild reaction conditions, with less energy requirement, avoiding toxic products generation and traditional chemical processes (Khare and Prakash 2017). This offers an energy-efficient, economical, clean and green bioprocess ensuring environmental sustainability, health, and socio-economic development (Khare 2021).

Diverse ranges of enzymes are oxidoreductase, laccases, peroxidases, lignin peroxidases, manganese peroxidase, tyrosinases, azoreductase, oxygenases, etc., that have efficient use in degrading organic pollutants. The extracellular or cell-free enzymes either partially purified or purified forms have promising application in management and degradation of organic pollutants in wastewater. However, cell-free enzymes used for bioremediation at the industrial scale may face certain problems. To circumvent the problems of free enzyme, immobilization techniques are utilized which enable enhanced catalytic activity, storage, and operational stability, including reusability of enzyme molecules (Prakash and Khare 2015). Moreover, advances in enzyme technology provide nanoscaffolds of enzyme for bioremediation of pollutants which are of serious concern to the environment and human health.

This chapter intends to provide an overview of organic pollutants present in wastewater and their impact on the environment and human health. It discusses about bioremediation strategy for mitigating toxic environmental contaminants. Further, the chapter gives an insight on enzymatic bioremediation as greener, cleaner and sustainable alternative for efficient management and detoxification of organic pollutants in wastewater. The chapter also highlights the current frontiers in arena of enzyme technology, compounded with immobilization and stabilization of enzyme molecules on various nanostructures in detail, and their potential application for bioremediation purposes.

## 15.2 Organic Pollutants

The wastewater discharge from industries, agricultural drainages, and domestic activities are major contributors to environmental pollutants into the water. In general, pollutants are inorganic, organic, biological, and radioactive substances (Bhomick et al. 2017). The effluents discharged from the textile, food, paper, agrochemicals (pesticides and herbicides), and petrochemical industries are the major source of organic compounds. The organic pollutants include phenolic compounds, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organic dyes, pharmaceutical compounds, personal care products, herbicides, pesticides, etc.

Some of these pollutants are grouped as persistent organic pollutants (POPs). These are man-made organic chemicals and is persistent in nature for several decades. POPs are the class of halogenated organic compounds that have strong bond between carbon and halogens (Cl, Br, F) owing to their persistence nature, resistant to biodegradation, chemical degradation, and photolytic reactions (Guo

**Table 15.1** List of persistent organic pollutants

| Persistent organic pollutants | Annexure |
|---|---|
| Pesticides | Annex B |
| • DDT (dichlorodiphenyl trichloroethane) | Annex A |
| • Aldrin | Annex A |
| • Dieldrin | Annex A |
| • Endrin | Annex A |
| • Heptachlor | Annex A |
| • Chlordane | Annex A |
| • Mirex | Annex A |
| • Toxaphene | |
| Industrial chemicals | Annex C |
| • PCBs (polychlorinated biphenyls) | Annex A and Annex C |
| • HCBs (hexachlorocyclohexane) | |
| Industrial by-products | Annex C |
| • PCDD (polychlorinated dibenzodioxins, known as dioxins) | Annex C |
| • PCDF (polychlorinated dibenzofurans known as furans) | |

et al. 2019). These are grouped as pesticides, industrial chemicals, and industrial by-products. Initially, twelve persistent organic pollutants commonly known as dirty dozen were included under these groups summarized in Table 15.1 (Qing Li et al. 2006; Zacharia 2019; UNEP n.d.). Many researchers have investigated and highlighted the threats caused to the human health and environment due to various emerging POPs over a time. Recently, 16 new chemicals are included in POP's list under the Stockholm Convention.

Pesticides are used for various non-agricultural purposes, beside agricultural purposes. It may enter the water resources, either through agricultural runoff or via industrial drainage and domestic wastewater. Toxicity of surface and ground water by pesticides like DDTs, dieldrin, aldrin, and endrin is of major concern due to its persistent nature (Sousa et al. 2018). However, even their use is restricted, as were rigorously used earlier for several years (Dujaković et al. 2010), and unlawful use gives an idea of existence of these compounds and their metabolites in the environment at the elevated concentration (Herrero-Hernández et al. 2017).

Annually synthesized dyes contribute to 700,000 tons, of which more than 100,000 dyes have commercial applications (Husain and Husain 2012; Martins et al. 2017). Industrial effluents account for 10% of total dyes utilized by various industries (Rauf and Ashraf 2012; Yagub et al. 2014; Ihsanullah et al. 2020). Major dye effluents is contributed by textile (54%), dyeing (21%), paper-pulp (10%), tanneries and paints (8%) along with dye manufacturing industries (7%) (Rauf and Ashraf 2012), which causes risk to the environment. The wastewater from paper and pulp industries contains large quantity of chlorinated organic compounds, chlorinated phenols lignin and its derivatives, including furans, dioxins etc. (Singh and Chandra 2019; Shankar et al. 2020).

Industrial chemicals, e.g., polychlorinated biphenyls (PCBs), are used like dielectric and coolant fluids in electric transformers and capacitors in industries. It is also used as additive in paints, plastics, and carbonless copy paper (Thakur and

Pathania 2020). PAHs are the group of hydrocarbons having frequent use in the production of various dyes, plastics, pesticides, and medicines (US-EPA 1998). Beside, steel mills, aluminum plants, coke ovens, oil refineries, coal and gasification plants are other sources of PAHs (Al-Hawash et al. 2018).

These organic compounds present in wastewater discharge is characterized by higher total dissolved solids (TDSs), biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total suspended solids (TSSs) (Singh and Chandra 2019). These organic pollutants increase freshwater's turbidity, which leads to eutrophication, posing adverse impact on water ecosystem. The augmented concentration of recalcitrant organic pollutants is of crucial importance due to their noxious, semi-volatile nature, lower biodegradability and solubility in water with elevated bioaccumulation causing health hazards (Bhomick et al. 2017; Bharagava et al. 2019).

## 15.3 Impact on Environment and Human Health

POPs are most lethal environmental contaminant. These chemical compounds are of global concern for environment and humans owing to higher toxicity, persistent nature, and vulnerability. These are less prone to biodegradation, environmentally mobile, and lipophilic in nature. This enables their bioaccumulation in the fat tissues of an organism, leading to biomagnifications (Katsoyiannis and Samara 2005). POPs are also insoluble or sparingly soluble in water. Their concentration is found elevated in the tissue of an organism at the higher trophic level, in contrast to the environment. Persistent organic pollutants ubiquitously occur in different components of environment, including fresh and marine water as the major reservoir. The distribution of organic pollutants and their mobility is regulated by physico-chemical properties of chemicals, climatic and localized weather conditions including the removal process (Foreman et al. 2000).

The environmental factors like precipitation, wind speed, solar radiations, and temperature also regulate the fate and transport of POPs in the environment (Gaur et al. 2018). Figure 15.1 depicts the fate of organic pollutants in the environment. POPs which are recalcitrant and highly persistent can travel over a long range of distance, and their residues detected far beyond the area of primary exposure/release (Farrington and Takada 2014). Hence, these are menace to the environment and humans. Contrarily, POPs also cause temperature change, altering precipitation, salinity, ice melt, and organic carbon cycle along with the food webs and lipid dynamics. These POPs exhibit grasshopper effect, which involves their movement from hot to cool weather condition. Further, it deposits in extremely cool environment, where it may evaporate upon increase in temperature. Consequently, this cyclic movement of POPs results in the global warming (Persson et al. 2005; Wöhrnschimmel et al. 2013).

Human beings are exposed to persistent organic pollutant existing in the environmental medium (air, water, soil, and food) through diverse routes. This includes

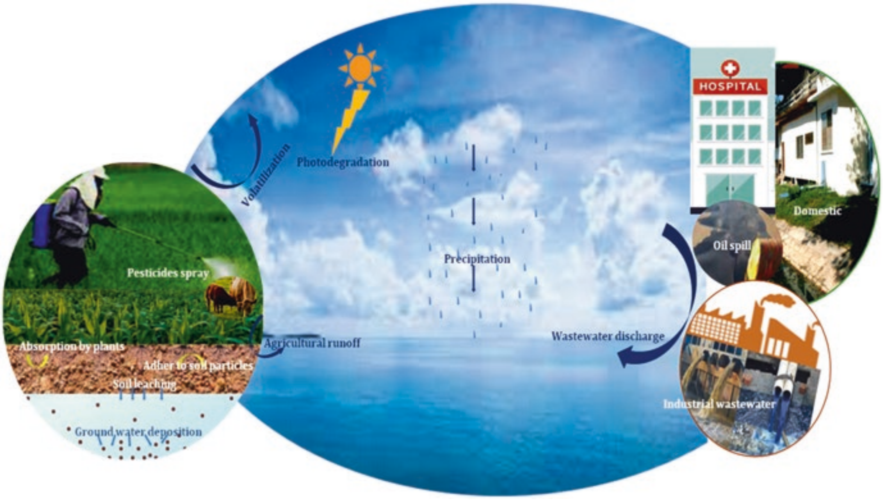

**Fig. 15.1** Fate of organic pollutants in environment

ingesting the contaminated food, inhalation, and through skin contact (Abhilash and Singh 2009). Beside the chemical nature of pollutants, their bioavailability also depends on the environment and nature of an organism. The toxicological impact of POPs causes adverse effect on human health. These are carcinogenic, neurotoxic, endocrine disrupter, susceptible to dysfunction of endocrine and reproductive system, and causes immune dysfunction, including birth defects (Zacharia 2019; Ali et al. 2014). POP's exposure at the elevated concentration shows problem of obesity and dyslipidemia (Ugranli et al. 2016; Fujii et al. 2007). Obesity may also cause exposure of other health-related problems like cancer, osteoarthritis, cardiovascular, apnea, etc. (Thakur and Pathania 2020).

Agricultural farm is a key source of POPs exposure to animals and humans. The POPs such as pesticides escape from the soil and plant surface via volatilization (Scholtz et al. 1993; Benjey 1993). These can persist until they end up in complete degradation. The long-term effect of pesticides on agricultural land could impose significant change making it unsuitable for farming and other uses. This upon soil leaching contaminates the ground water. It may accumulate in the bottom of the water resources via agricultural runoff, atmospheric deposition, and effluents discharge from various industries and domestic household work (Thakur and Pathania 2020). Further, uptake of pesticides by the aquatic organisms, such as fishes including other animals, cow, buffaloes, etc., causes biomagnifications of these pollutants over a wider range.

Rachel Carson highlighted the adverse impact of dichlorodiphenyltrichloroethane (DDT) an organochloride pesticide used in agriculture to control insects in his famous book "Silent Spring." Several years ago, the use of DDT is phased out but still their residues and illicit use suggest their presence in the environment. DDT can be transformed into dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) in nature, which is equally persistent. DDT and its metabolites being insoluble in nature enable their bioaccumulation easily in aquatic organisms and enter the food web affecting the wildlife, birds, and other organisms. It causes eggshell thinning in birds, which led to decline in peregrine falcon, bald eagle, brown pelican, and osprey (Gebresemati and Sahu 2016; Neitsch et al. 2016; Balawejder et al. 2016).

DDT and their metabolites are carcinogenic which cause cancer of breast (Mathur et al. 2002) and other organs. These are endocrine disrupters, and alter the reproductive potential and development of embryo or fetus in humans (Thakur and Pathania 2020). However, chlordane shows lethal effects on fishes and birds and may cause their death. These are carcinogenic to humans and affect their immune system. Human beings exposed to heptachlor through food and drinking water, show neurological problems, irritation, dizziness, and salivation. This also affects the blood, causing gastrointestinal problems. However, endrin causes toxicity to the fish when present in augmented concentration in the water (Thakur and Pathania 2020).

The untreated or partially treated industrial chemicals discharged in the aquatic ecosystem are of serious concern for biota and environment. Lower dosage of PCBs shows toxicity in fish causing spawning failure. PCBs also cause infertility and immune system suppression in wild animals (Jepson et al. 2016; Smith et al. 2007). It causes problem of nails pigmentation, mucous membranes, fatigue, nausea, vomiting, and edema of eyelids. Humans are prone to pancreatic cancer (Alharbi et al. 2018) and cardiovascular problems such as high blood pressure, increased triglycerides and metabolic syndrome. The exposure of elevated concentration of PCBs in pregnant women shows developmental delays and altered behavior of children (Thakur and Pathania 2020). These hydrocarbons such as PAHs and PCBs being persistent compounds are of critical concern upon bioaccumulation, due to their carcinogenic and mutagenic nature (Perelo 2010).

Petroleum hydrocarbons float on the surface of aquatic environment. PAHs may enter the aquatic ecosystem either directly through the oil spills, or indirectly via terrestrial runoff and atmospheric deposition. The physical and chemical properties are mainly responsible for their persistent nature. Owing to complex structure, higher halogenated and hydrophobic compounds tends to have lower water solubility, which provides ease for their adsorption, and get associated with the sediment particles (Perelo 2010; Giovanella et al. 2020). Petroleum hydrocarbons viz., PAHs can be mutagenic, carcinogenic, toxic to immune system and teratogenic to different life forms (Varjani et al. 2017). It has higher affinity for biomolecules viz., DNA, RNA, and protein and consequently results in mutations and tumors formation, affecting the dermal layer and other organs (Varjani 2017). Moreover, acute effects of these organic pollutants have problems like nausea, eye and skin irritation. However, the chronic effects show organ damage which includes kidney, lung, and liver. This can also cause immune system toxicity and defects in fetus development (Varjani et al. 2017; Giovanella et al. 2020).

On the other hand, dioxins and dioxin-like compounds such as PCDDs, PCDFs and dioxin-like PCBs (DL-PCBs), known as priority substances are present in the environment for decades. These show toxicity in organisms, like carcinogenicity, neurotoxicity, dermal problems, including reproductive and developmental defects (Eqani et al. 2015). Even the problem of diabetes is complained among the children due to PCDDs and PCDFs (Muñoz-Arnanz et al. 2016; Lammel et al. 2016). Moreover, dioxins are also associated with certain cardiovascular problems such as elevated triglycerides, high blood pressure, glucose intolerance, and metabolic syndromes (Thakur and Pathania 2020).

Apart from this, the wastewater from pulp and paper industries containing heavy load of organic pollutants is of critical concern to aquatic environment and other organisms. It is a serious problem for humans and animals as they use surface and underground water as the source of drinking water (Singh and Chandra 2019). These are mutagenic, carcinogenic, clastogenic (Ericson and Larsson 2000) and endocrine disrupter, which causes health hazards. Besides, it is also lethal to fishes, and show harmful effect on living zooplanktons and phytoplankton deteriorating the aquatic environment (Singh and Chandra 2019).

Likewise, industrial dyes discharged as industrial effluent or domestic waste have deleterious effect on water and human life. It alters the aesthetic value of water resources, with change in color of water, inhibiting sunlight penetration. This led to decline in the photosynthetic activity, plant growth, and causes damage to the aquatic organism (Zaharia et al. 2009). Dyes deteriorate the water quality causing eutrophication, which leads to augmented BOD and COD. This interferes with ecological conditions of living flora and fauna. Dyes and their metabolites are persistent and may enter the food chain showing noxious effect such as carcinogenic, mutagenic, neurotoxicity and dermal problems such as skin irritation in human beings (Carmen and Daniela 2012).

## 15.4 Bioremediation

Bioremediation cascades afford development, commercialization, and application of processes or products to manage organic pollutants (Kirchhoff 2003). It is environment friendly, sustainable, and economically efficient bioprocess. This helps in restoring the polluted sites containing various pollutants, and reduces the risk of pollution at the source. Therefore, it promises greener and cleaner technology with public acceptance contrary to other physical and chemical methods. Bioremediation is of two basic types viz., on-site or in situ and ex situ as considered by some of the researchers, depending upon the site of implication, total expenses, nature and concentration of pollutants. Besides, physico-chemical parameters like temperature and pH, nutrient and oxygen concentration including other abiotic factors also play a key role in achieving effective bioremediation process (Azubuike et al. 2016).

Ex situ bioremediation is a cost intensive technique, which covers additional expense of excavation. The nature of pollutant, degree and depth of performance along with the geographical site of pollution are other key factors which affect the bioremediation process (Philp and Atlas 2005). Contrarily, on-site or in situ bioremediation strategy is economical involving on-site installation of equipment to remove pollutants with diminished damage to the environment. The aquifers used as bioreactor for the removal of pollutants from groundwater, enable cost effective and energy-efficient process (Majone et al. 2015; Ikehata et al. 2016; Zhang et al. 2017). Besides traditional approaches which involve external equipment, the in situ bioremediation finds promising role in treating noxious pollutants at water surface, groundwater, drinking water, and industrial effluents (Brierley 1990; Chapelle 1999; Wagner-Döbler 2003).

Bioremediation is a complex process, which involves biotransformation, biodegradation, and mineralization. In the process of biotransformation, hazardous organic and inorganic pollutants are converted to less or nonhazardous form. However, the process of biodegradation involves breakdown of complex organic compound into simplified subunits. Conversely, mineralization led to complete breakdown of organic compound into inorganic form viz., $CO_2$ or $H_2O$ (Saxena and Bharagava 2017; Pilon-Smits 2005). Bioremediation involves either use of whole cell or the cell-free enzymes commonly known as white biotechnology (Alcalde et al. 2006). Although, various strategies are available for biodegradation and bioremediation of toxic pollutants; the nature (homogenous or heterogenous) and the concentration of pollutant is considered as the crucial factor before employing a specific type of bioremediation. Moreover, adopting single remediation strategy is sometimes not so efficient in restoring the degraded environment (Azubuike et al. 2016). Bioremediation broadly categorized into three groups, depending upon the types of biological agent (Fig. 15.2). Bioremediation involves implementing plants (phytoremediation), microbes like bacteria, fungi (mycoremediation) (Zhang et al. 2017) and their by-products like enzymes (enzymatic bioremediation) to detoxify diverse

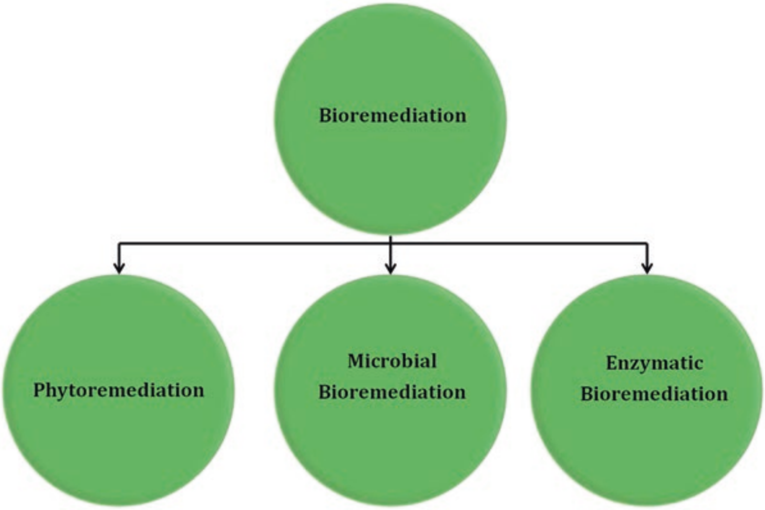

**Fig. 15.2** Types of bioremediation

organic waste (Kulshreshtha 2012) as efficient, environmental benign and sustainable bioprocess.

Phytoremediation has attracted significant interest as cleanup technology, which utilizes the ability of plants and their associated microbes to mitigate noxious compounds. Plants and rhizospheric microbes degrade the environmental pollutants (Pilon-Smits 2005). Generally, plants uptake water soluble organic pollutants through their roots. This led their translocation to various parts of the plant tissues; where it may be metabolized, sequestered, or volatilized. While, the degradation of organic wastes is not expedite process and leads to accumulation of these noxious compounds in plants (Van Aken 2008). This can cause organic pollutants exposure of environment and through food chain; it ultimately affects the human beings. Further, disposal of plants accumulated with these toxic organic pollutants is another serious concern (Abhilash et al. 2009). Apart from this, the problem of root depth, bioavailability of pollutants and slower rate of degradation hamper their application for large-scale detoxification of organic pollutants.

On the other hand, microbial bioremediation utilizes the enzymatic potential of bacteria, fungi, and algae for abatement of toxic organic pollutants in the environment. Different parameters such as (1) organism type, (2) type of contaminants, and (3) geological and chemical conditions at the polluted area regulate the fate of bioremediation (Kumar and Bharadvaja 2019). Microbes offer plethora of enzymes as natural resources for remediation of organic pollutants. Even microbes present in the polluted environment have the ability to detoxify the pollutants (Azubuike et al. 2016). Nevertheless, the major challenges are the adequate environment requirement for the growth and activity of microbes (Verma and Jaiswal 2016). Temperature, pH, nutrient availability, and presence or absence of oxygen influence the growth of microbes (Kumar and Bharadvaja 2019; Ronen and Abeliovich 2000). This provides ease for rapid degradation of organic pollutants by utilizing these noxious products as energy source for their growth (Watanabe 2001). Moreover, organic pollutants under aerobic respiration are mineralized into water and carbon dioxide (Ojuederie and Babalola 2017), while the final product of anaerobic respiration is carbon dioxide, ethanol, or lactic acid (Kumar and Bharadvaja 2019).

Although, microbes have application in detoxifying various organic compounds from the wastewater, but these are inefficient in treating certain phenolic compounds, dyes, and pharmaceutical wastes. These compounds resist microbial remediation, owing to lack of sufficient amount of enzymes produced by the microbes, and diffusional restriction for substrate transport (Thwaites et al. 2018). In recent few decades, development in enzyme technology and immobilization techniques for stabilization of enzyme molecules have opened new opportunities for enzymatic bioremediation of organic pollutants. This avoids the use of microbial whole cell. The subsequent section of this chapter further discerns about the enzymatic bioremediation.

## 15.5 Enzymatic Bioremediation: A Green Bioprocess

Implementing enzymes based green bioprocess is a novel tool for bioremediation, which provides environment friendly and sustainable alternative (Singh and Walker 2006). It generally operates under mild reaction conditions in aqueous environment, with lower activation energy (Prakash and Khare 2019) and speeds up the reaction involving complete breakdown of organic substrate compared to non-enzymatic reaction (Fan and Krishnamurthy 1995). Enzymes either partially purified or purified forms both have their extensive application in bioremediation. However, generally whole cell use is hampered due to continuous supply of fresh inoculums, maintenance and transfer of microbial culture, including aeration, and nutritional requirements (Rayu et al. 2012).

Moreover, certain pollutants are noxious to the biological agents used. Therefore, require attuned microbes and prolonged time for the decontamination. These constraints have boosted to implement cell-free enzymatic strategy for efficient bioremediation. This provides ease for small sized enzyme molecules to come in contact of contaminants with high mobility (Rao et al. 2010), possessing higher activity, enhancing the rate of degradation, favoring less tedious and efficient bioprocess with sustainable approach. Hence, this enzymatic reaction promises energy-efficient and highly economical bioprocess, minimizing the risk of waste production (Sheldon and van Pelt 2013). However, application of enzymatic bioremediation technology requires understanding the key role of enzymes, their nature and mechanism of action.

### *15.5.1 Enzymes Used in Bioremediation of Organic Pollutants*

Oxidoreductase group of enzymes viz., peroxidase, laccases, and tyrosinase have key role in bioremediation of organic pollutants from wastewater. Redox enzymes have extensive use for bioremediation of phenolic compounds, azo dyes, PAHs, PCBs, etc. Laccases and peroxidase are the most common enzymes used to remove phenolic and non-phenolic aromatic compounds present in the wastewater. However, laccases represent a better catalyst over peroxides that catalyze the reaction in the absence of $H_2O_2$, instead of using oxygen (Alshabib and Onaizi 2019).

Laccase is a copper containing enzyme, grouped as type 1, type 2, and type 3. Mechanism of laccases reaction involves electron extraction from their substrates with generation of an unstable intermediate as “free radical.” The product of laccase-catalyzed reaction is mostly unstable. These undergo an additional reaction which may involve polymerization, disproportionation and/or hydration (Osuoha and Nwaichi 2021). The enzymatic catalysis of laccases in prior reviewed by many researchers in detail (Bourbonnais et al. 1997; Robles et al. 2000; Alshabib and Onaizi 2019). Laccases are used to remove bisphenol A and diclofenac (Demarche et al. 2012; Sathishkumar et al. 2012). Laccases catalyze degradation of phenols that involves oxidation of one electron by the type 1 (T1) copper site. Subsequently, the electrons are transported to T2 and T3 copper sites, where further oxygen is reduced to form water molecules (Alshabib and Onaizi 2019).

Legerska et al. reported laccases mediated degradation of azo dyes, which involve bond oxidation and their transformation to less toxic form (Legerská et al. 2016). Laccases are directly used to degrade dyes. This involves dechlorination of chlorophenols, aromatic rings cleavage, and mineralization of polycyclic aromatic hydrocarbons (Madhavi and Lele 2009). Chlorinated compounds like tetrachloroethene and polychlorinated biphenyl, which pollute underground water, are mainly degraded using oxidoreductase enzymes. Mono- and dioxygenases are strong dehalogenating agents (Furukawa 2000; Schultz et al. 2001). The ethenemonooxygenase and biphenyl dioxygenase enzymes could be successfully used for large-scale industrial applications (Younus 2019).

Another important enzyme is horseradish peroxidase (HRP), which operates under broad ranges of pH and temperature in presence of other pollutants found in municipal wastewaters (Melo et al. 2016). The enzymes require $H_2O_2$ during catalysis and their concentration regulates the reaction (Alshabib and Onaizi 2019). Enzyme peroxidase oxidizes phenolic compounds to produce phenoxy radicals, compounded to form oligomeric and polymeric products (Ward et al. 2001a, 2001b). The polymeric products easily aggregate and precipitate, that enables detoxification and treatment of industrial wastewater (Husain 2006). Ely et al. reported rapid detoxification of phenols (99%) within 35 min from a biorefinery wastewater using HRP (Ely et al. 2017). In addition, peroxidases also have potential application in degrading Bisphenol A (BPA) and other aromatic compounds (Escalona et al. 2014; Husain 2006).

On the other hand, enzyme lignin peroxidases (LiP) mineralize various aromatic compounds and oxidize array of polycyclic aromatic and phenolic compounds (Karam and Nicell 1997; Wesenberg et al. 2003). Lignin peroxidases are superior catalyst compared to laccases and HRP. LiP are widely used for degradation of polycyclic aromatic hydrocarbons (PAHs) (Hammel et al. 1992; Bogan and Lamar 1995), phenolic pollutants (Aitken et al. 1989), and benzo(a) pyrene (Sanglard et al. 1986). Moreover, enzyme LiP and ligninase both have potential to oxidize various chlorinated compounds in the presence of $H_2O_2$ (Husain 2006). Manganese peroxidase (MnP) is also an important enzyme that degrade PAH and phenolic compounds. It functions similar to peroxidases but requires Mn (II) for its activity. MnP have promising role in complete degradation of anthracene (Eibes et al. 2005). MnP along with LiP also have potential to cause detoxification of dioxins (Qayyum et al. 2009).

Apart from peroxidases, polyphenol oxidases (PPOs) play a key role in degrading aromatic pollutants from polluted sites. Enzymes have the ability to attack wide range of substrates and catalyze the detoxification of these pollutants, even if present in trace amount at the polluted sites (Husain and Jan 2000). Polyphenol oxidase from brinjal was used to treat various textile and other non-textile dyes (Ali and Qayyum 2007). In general, enzyme-based bioremediation of dyes is influenced by various factors such as oxygen transfer, pH, temperature, structure of dye, presence of redox mediators, including concentration of enzyme and dye. However, Ali and Qayyum (2007) showed efficient removal of dyes alone and the mixture of dyes contaminated wastewater without the use of any redox mediator.

Azoreductase enzymes have use in decolorization of azo dyes, and their metabolic product contains aromatic amines. The study deciphers the role of azoreductase, which exhibits reductive cleavage of the azo bond of methyl red and other related azo dyes (Moutaouakkil et al. 2003). On the other hand, tetrahydrofuran monooxygenases (THF MOs) enzyme has potential application for the removal of dioxane an emerging contaminant of water resources. The enzyme mainly catalyzes the reaction by hydroxyl group insertion at the α-carbon position of dioxane. This eventually leads to cleavage of the high-energy ether bond known as "α-hydroxylation" (Deng et al. 2018).

Dehalogenase is another important enzyme, which enables degradation of halogenated compounds. It functions by cleaving the carbon–halogen bonds that accounts for toxicity of halogenated pollutants. The number of halogenated compounds includes chloro- and hydroxychloro-benzoate, PCBs, pentachlorophenol, chlorinated phenoxyacetic acids, lindane, chloroalkanes, chlorophenylacetate, haloaromatic compounds, haloalkanes, haloalkanoid acid compounds, bromo and chloroalcohols, etc. that are degraded by the help of these enzymes (Swanson 1999; Gianfreda et al. 2016). Besides, enzyme lipase also has role in degradation of hydrocarbons.

### 15.5.2 *Major Challenges*

The bioremediation of organic pollutants using free enzyme faces certain challenges, which are as follows:

- Higher cost involved in enzyme production
- Short lifespan
- Higher sensitivity towards adverse reaction conditions
- Lack of operational and storage stability
- Lack of enzyme recovery
- Cost intensive process

## 15.6 Advances in Enzyme Technology: A Nanobiocatalyst for Bioremediation

Recent advances in the area of nanotechnology have provided opportunity for implementing nanomaterials integrated with biotechnological tool (Prakash and Khare 2019) for rapid and efficient bioremediation. Enzyme immobilization on nanomaterials helps to circumvent the problems faced by the free enzyme molecules. Over past few decades, enzymes immobilized on various traditional matrices were used for bioremediation of environmental pollutants. However, these matrices have certain lacunae, which are overcome by using nanomatrices. In general, nanomatrices used for enzyme immobilization alter the properties of nanobiocatalyst. Nanomaterials possess size of nanoscale range (1–100 nm), which enable manipulating enzyme at nanoscale with uniform size distribution of enzyme. This provides improved optical and electronic properties along with distinct surface chemistry. High surface area to volume ratio of these nanostructures provides high enzyme loading, with enhanced catalytic activity, enzyme stability such as mechanical, thermal, storage, operational stability, and reusability (Prakash and Khare 2019). This increases the half-life of enzyme molecules and enhances their reusability, thereby reducing the cost of operation (Rayu et al. 2012). However, compared to simultaneous adsorption and enzymatic membrane bioreactors (Zdarta et al. 2019), the immobilization is economically feasible and efficient bioprocess. Hence, enzyme immobilized on nanomatrices provides nanobiocatalyst with improved properties for effective bioremediation of organic pollutants promising greener, and cleaner alternative with sustainable approach (Fig. 15.3).

Enzyme immobilization could be attained by various strategies viz., physical adsorption, crosslinking, entrapment/encapsulation and covalent interaction (Prakash and Khare 2019). Several studies have reported the immobilization of enzyme molecules on different nanostructures and their utilization for breakdown of recalcitrant organic waste present in the wastewater. Lai et al. reported laccases crosslinked to polymethacrylate/carbon nanotubes used for decolorization of dyes. Moreover, it also revealed excellent reusability with retained enzymatic activity of 90% even after 10 repeated cycles of reuse. This suggests efficient application of laccase immobilized on nanotubes in removing azo dyes from wastewater (Lai et al. 2019). In another study, laccases immobilized on metal oxides like ZnO and $MnO_2$ nanoparticles were used to remove Alizarin Red S (ARS), and depicted their potential application as adsorbent in wastewater treatment (Rani et al. 2017).

Wang et al. deciphered the role of laccase immobilization onto magnetic mesoporous silica nanoparticles for phenol degradation from coking wastewater. Immobilized enzyme possesses two-fold higher enzyme activity, and enhanced stability with 71.3% degradation rate even after 10 successive batch treatment. This suggested cost effective and efficient bioprocess of bioremediation of phenols (Wang et al. 2012). In recent study, halloysite nanotube and magnetic nanoflowers immobilized laccase revealed their potential application for efficient removal of various dyes and bisphenol A. These have higher reusability of 11th cycle with 33% and 5th cycle with 95% degradation efficiency, respectively (Kadam et al. 2018; Fu et al. 2019). Magnetic nanoflowers exhibited rapid degradation, that provided ease for recovery of nanobiocatalyst by applying external magnetic field (Fu et al. 2019), promising efficient and economical bioprocess. Ardao et al. (2015) depicted the potential of magnetic laccase-biotitania (lac-bio$TiO_2$), a biocatalyst for remediation of endocrine disrupting substances such as bisphenol A, 1,7α-ethinylestradiol, and diclofenac in a mixture of six model EDCs with higher catalytic activity, enhanced stability, reusability, and ease of recovery.

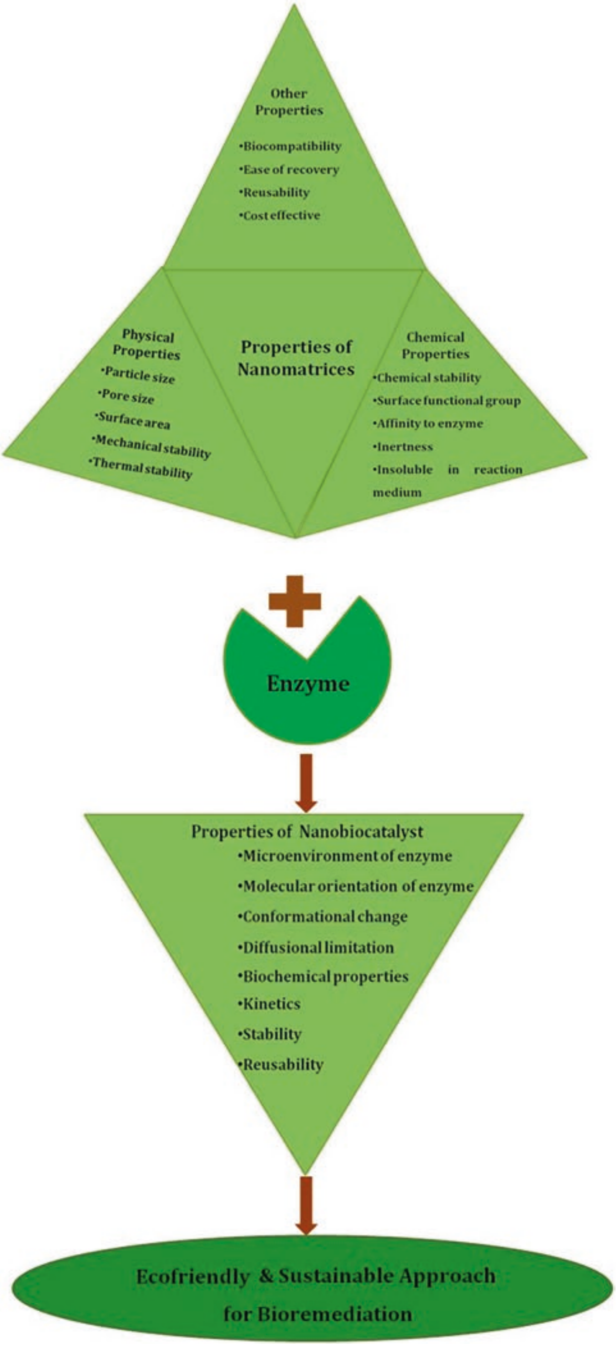

**Fig. 15.3** Nanobiocatalyst for effective bioremediation

In another study, magnetic biocatalyst was prepared by immobilizing laccase as crosslinked enzyme aggregates (MAC-CLEAs) on amine functionalized magnetic nanoparticles. This nanobiocatalyst is used for bioremediation mixture of pharmaceutical compound in batch process. It possesses excellent storage stability over a year with enhanced catalytic activity, reusability, and ease of recovery to remove various pharmaceutical compounds from wastewater (Kumar and Cabana 2016). Recently, tyrosinase immobilized on functionalized magnetic iron oxide nanoparticles, as biocatalysts were used for degrading phenols present in synthetic wastewater (Abdollahi et al. 2018). The magnetic biocatalyst can be promising alternative over a catalyst used in conventional treatment processes for bioremediation of organic pollutants.

Recently, study on horseradish peroxidase (HRP) immobilized on carbon nanosphere was used to remove phenolic compounds. Carbon nanosphere is a cost effective support material, which upon enzyme immobilization prevents protein denaturation and has augmented enzyme stability over broad range of pH and temperature. It revealed augmented catalytic activity and excellent storage stability with efficient removal of various phenols (Lu et al. 2017). Qiu et al. (2009) explored nanoporous gold (NPG) for lignin peroxidase (LiP) immobilization. Moreover, enhanced catalytic activity of LiP involved in situ release of $H_2O_2$ by co-immobilization of glucose oxidase. This co-immobilization system provided effective dye decolorization with excellent catalytic activity, storage stability and reusability (Qiu et al. 2009). Recent study by Ali et al. reported immobilization of peroxidase from ginger on amino-functionalized silica coated $TiO_2$ nano-composite (AF-$SiO_2$-$TiO_2$NC) and their role in rapid degradation of dye in batch process. The study explored immobilized enzyme having augmented catalytic activity, stability, biocompatibility, and reusability for their application in bioremediation (Ali et al. 2017). Table 15.2 summarizes the details of enzyme immobilized on various nanostructures and their role in removal of organic pollutants.

## 15.7 Conclusion and Future Prospects

In present scenario, the problem of organic pollutant has escalated rapidly due to various anthropogenic and industrial activities. This creates a serious nuisance for the environment, animals, and humans. The urge is to achieve environmental sustainability by adopting clean and eco-friendly alternatives to treat and manage various organic pollutants. Although, the chapter discusses in detail the aspect of bioremediation for abatement of toxic organic pollutants in wastewater. Despite the success of various biological agents, viz., plants, microbes, or the enzymes to nanoscaffolds of enzymes, as green and clean bioprocess for bioremediation, there are significant numbers of limitations considering each of these methods. The major problems include technical challenges, practical implication, and higher operational cost. Therefore, the need is to resolve such challenges, prior these methods find their wider implication and public acceptance. Among wide range of bioremediation techniques, nanoscaffold of enzyme is an emerging highly efficient strategy owing

**Table 15.2** Enzyme immobilized on various nanostructures for removal of organic pollutants

| Enzyme | Support material | Organic pollutant | Removal (%) | Reference |
|---|---|---|---|---|
| Laccase | Magnetic mesoporous silica nanoparticles | Phenol | 98.5 | Wang et al. (2012) |
| Laccase | bio$TiO_2$ particles | 1,7-α-ethinylestradiol<br>Bisphenol A<br>diclofenac | 92<br>85<br>54 | Ardao et al. (2015) |
| Laccase | ZnO nanoparticle<br>$MnO_2$ nanoparticle | Alizarin Red S (ARS) | 95<br>85 | Rani et al. (2017) |
| Laccase | Chitosan functionalized supermagnetic halloysite nanotube | Direct Red 80 (DR80) | 87 | Kadam et al. (2018) |
| Laccase | Magnetic nanoflowers | Bisphenol A | 100 | Fu et al. (2019) |
| Laccase | Polymethacrylate/carbon nanotubes | Methylene blue<br>Orange II | 96<br>74 | Lai et al. (2019) |
| HRP | Carbon nanospheres | Phenol<br>Paracetamol<br>Catechol<br>*p*-Chlorophenol<br>2,4-Dichlorophenol<br>1,4-Methoxyphenol<br>Bisphenol A | 45.8<br>98.2<br>100<br>31.2<br>56.3<br>44.6<br>15.3 | Lu et al. (2017) |
| Lignin peroxidase coimmobilized glucose oxidase | Nanoporous gold | Pyrogallol red<br>Fuchsine<br>Rhodamine B | 87.2<br>84.6<br>75.5 | Qiu et al. (2009) |
| Ginger peroxidase | AF-$SiO_2$-$TiO_2$NC | Acid Yellow 42 | 90 | Ali et al. (2017) |
| Tyrosinase | MNPs | Phenol | 78 | Abdollahi et al. (2018) |
| Laccase | MAC-CLEAs | Menfenamic acid<br>Acetaminophen<br>Diclofenac<br>Atenolol<br>Diazepam<br>Epoxycarbmazepine<br>Fenofibrate<br>Trimethoprim<br>Ketoprofen<br>Indometacin | 99<br>85<br>85<br>74<br>60<br>55<br>54<br>47<br>46<br>37 | Kumar and Cabana (2016) |

to higher catalytic activity, biocompatibility, stability, and reusability promising highly efficient, economically feasible green bioprocess with sustainable approach. Hence, the recent advances in nanotechnology have created boon for enzyme technology, which provides nanobiocatalyst for environmental bioremediation. Still, the future prospect in the area of bioremediation provides exciting opportunities to explore the area of metagenomics, enzyme engineering, and nanotechnology to overcome the limitations and enhance the enzyme efficiency in a bioreactor and polluted environment.

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# Chapter 16
# Nanomaterial Hybridized Hydrogels as a Potential Adsorbent for Toxic Remediation of Substances from Wastewater

**M. Maria Rahman, Hirotaka Ihara, and Makoto Takafuji**

**Abstract** In the twenty-first century, water contamination has become a severe global concern due to the discharge of huge amount of untreated textile effluents in water that causes detrimental effects on aquatic environments and human life. Therefore, the efficient treatment of these toxic substances from effluent water has a pressing demand before being disposed into water bodies for sustainable development. Hydrogels are networks of crosslinked hydrophilic polymers, capable of absorbing and resealing enormous quantity of water. In the few decades, nanomaterials hybrid hydrogels have attracted huge attention owing to the tuneability of their properties including hydrophilicity, sensitivity, and functionality. These unique properties make them highly promising materials for adsorptive removal of multiple toxic pollutants including heavy metals, pesticides, phenolic compounds, and toxic dyestuffs from water. The insights of this chapter highlighted the efficiency of the nanomaterial hybridized hydrogels for remediation of toxic pollutants, more specifically the textile dye pollutants from wastewater.

**Keywords** Hydrogels · Nanocomposite · Water pollution · Toxic dyestuffs · Adsorption

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## 16.1 Introduction

Water is one of the most vital natural assets that have a direct impact on all living beings and natural atmosphere (Singh et al. 2020). The World Health Organization (WHO) reported nearly 844 millions of people have inaccessible to safe drinking water supply, and 159 million exclusively reliant on the surface of the earth water (World Health Organization 2019a). In addition, water hygiene will be the topmost universal public health challenges in the next decade (World Health Organization 2019b). Moreover, WHO also stated, that almost 1.7 million people pass away owing to water contamination, and four billion people suffer diverse health issues per annum because of waterborne diseases (Briggs et al. 2016). So, the safety of natural water resources is of great attention around the globe. Nowadays, the rapid expansion of textile industries and human activities generates huge amount of toxic pollutants including heavy metals, textile dyes, and agricultural wastes, resulting in water pollution (Kumar et al. 2020; Sanchez et al. 2019). Among the aforementioned pollutants, dyestuffs are considered as the topmost source for groundwater contaminants because of widespread used in textiles, pulp and papers, plastics, painting, tannery and pharmaceutical industries (Gupta and Suhas. 2009; Omran et al. 2016). There are numerous varieties of synthetic coloring materials including acidic, basic, disperse and reactive dyes, which has been used in different industries (Donkadokula et al. 2020). Generally, the textile dyes are toxic, highly carcinogenic, and non-biodegradable substances because of its complex chromogen–chromosphere chemical structure that makes it very stable against sun light and oxidation reactions (Mishra et al. 2021; Jabar et al. 2020). The disposal of untreated dyestuffs bearing water to the environment posed a serious threat to aquatic lives and ecosystem (Sahoo et al. 2019; Zhang et al. 2011). Therefore, it is necessary to treat dye effluent water before being releasing into the water source. Although during the past few decades, several techniques have been utilized for encapsulation of various dyestuffs from effluent water, including advanced oxidation (Muhammad et al. 2008), fenton–photophenton degradation (Rahman et al. 2010), photochemical degradation (Hasnat et al. 2007), adsorption (Rahman et al. 2014), membrane separation (Jedidi et al. 2011) and coagulation (Patel and Vashi 2012), and electrochemical treatment (Szpyrkowicz et al. 2001). Among the present treatment methods, adsorption process is one of the promising ways for encapsulation of contaminants from textile sewages water owing to the simplicity of fabrication, cost-effective, less energy consumption, high efficiency, and regeneration capability (Mahapatra et al. 2013; Rahman et al. 2021b; Katheresan et al. 2018). In recent times, several adsorptive materials have been reported for encapsulation of contaminants from effluents water, for example, carbon-based materials, metal oxides, zeolites, and nonporous silica (Omran et al. 2016; Kowsalya et al. 2015; Yang et al. 2015), but, owing to low adsorption rate and ability, longer equilibrium time and difficulty of reusability significantly restricted their applications (Ahmad and Kumar 2010). Thus, it is requisite to fabricate economical, high removal efficiency, and reusable materials for remediation of toxic substances from industrial effluents water.

Recently, polymeric hydrogels are very attractive and versatile soft materials, which are extensively applied for the encapsulation of contaminants from effluents water. (Hong et al. 2018; Salahuddin et al. 2018). Hydrogels are composed of three-dimensional crosslinked hydrophilic matrixes of polymer that is capable of keeping enormous quantity of liquids owing to the presence of hydrophilic functional groups namely hydroxyl (-OH), amino(-$NH_2$), carboxylic (-COOH), and sulfonic acid (-$SO_3H$) (Sharma et al. 2019, Rahman et al. 2021a, b). The structure and properties of hydrogels are easily tunable with respect to temperature, pH, ionic strength and interact with adsorbents (Khan and Lo 2016; Arami et al. 2006). Thus, hydrogels are known to use in several arenas, including effluents water treatment, tissue engineering, biomedical applications, contact lenses, wound dressing, chemical sensors, and catalysis (Zhou et al. 2018; Katsoulos et al. 2009; Tadsen et al. 2019). However, the majority of polymeric hydrogel has poor mechanical property that makes it difficult to be recycled and importantly limits its practical applications (Pan et al. 2017). In recent times, scientists are devoted to fabricate the hydrogels with higher mechanical strength (Wu et al. 2019). Generally, the mechanical property of hydrogels is reinforced by preparing double network hydrogel and a nanocomposite or nanomaterial hybridized hydrogel (Lu et al. 2019; Neghi et al. 2019). Among the hydrogels, nanomaterial hybridized hydrogels are most prominent to strengthen the properties of hydrogels. The nanomaterial hybridized hydrogels are engineered by incorporation of nanomaterial into the three-dimensional matrix of polymer via covalent or physical interactions. The combination of organic polymer and inorganic nanoparticles in the hydrogel network generates nanoparticle hybrid composite materials with excellent mechanical, thermal, and adsorption properties (Zhao et al. 2019). The extensive variety of nanoparticles, including carbon-based nanoparticles (graphene oxide, carbon nanotube), metal and metal oxide nanoparticles, and silica nanoparticles has been integrated into the matrixes of polymer to obtain diverse hybrid hydrogels (Hiew et al. 2019). Generally, the nanomaterial hybridized hydrogel can be fabricated by the following different methods: (1) Nanomaterials-dispersed hybrid hydrogel and (2) Nanomaterials-crosslinked hybrid hydrogel. Figure 16.1 illustrates the different scheme for preparation of nanomaterials hybrid hydrogels. The desired nanocomposite can fabricate by the nature of polymer matrix and nanoparticles. The nanoparticles can act as a crosslinker between polymer chains for formation and stabilizing of hydrogels (Thoniyot et al. 2015; Takafuji et al. 2011; Grzelczak et al. 2010) via physically or covalent bonding. The hydrogels fabricated using nanoparticles can interact synergistically resulting in exhibiting new properties including enhanced mechanical, thermal, electrical conductivity, optical, magnetic, self-healing, adsorptive and catalytic properties that are not present in the only organic polymer hydrogels (Zhao et al. 2019; Neghi et al. 2019).

More importantly, these unique features can be adjusted by changing of the environmental conditions. Therefore, these unique properties of nanoparticle-hybridized hydrogels make them most prominent in waste water remediation, particularly adsorptive remediation of toxic dyes from textile effluents water. However, the fabrication of hydrogels having expected functionalities has provided a unique avenue to design hybrid hydrogels for remediation of toxic substances from contaminated

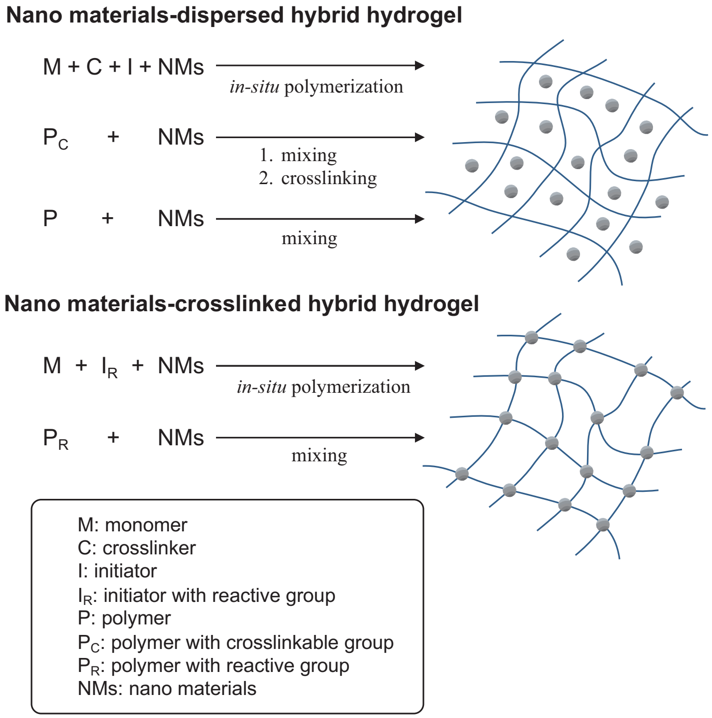

**Fig. 16.1** Strategy for preparation of nanomaterials-composed hybrid hydrogels

water. The main highlight of this chapter is to provide the recently developed nanomaterial hybridized hydrogels for remediation of organic dyes from wastewater. In addition, the opportunities and challenges in desirable features of these hybrid hydrogels are also presented.

## 16.2 Carbon Nanomaterial-Hybridized Hydrogels for Wastewater Treatment

Carbon nanomaterials are very promising materials because of their diverse structure and morphology while being entirely composed of carbon atom, which are covalently bonded in a hexagonal lattice ($sp^2$). The carbon nanomaterials including graphite, graphene, graphene oxide (GO), carbon nanofibers (CNFs), and carbon nanotubes (CNTs) are incorporated onto polymer matrix of hydrogels via chemically or physically. These composite materials exhibit multi-functionalities and outstanding properties including thermal, optical, and mechanical properties, which enable these hybrid materials to utilize in numerous arenas to remediation of environmental and energy issues (Papageorgiou et al. 2017; Siwal et al. 2020; Dutta et al. 2019). To date, GO hybrid hydrogels have gained great attention owing to the numerous reactive groups including hydroxyl, epoxide, carboxylic, and carbonyl groups present on to binary edges of the nanosheets, which could be simply assembled into three-dimensional honeycomb structures having pores size of nanometers to micrometers. Thus, GO is an effective adsorbent material for encapsulation of toxic organic dyes (Banerjee et al. 2019; Li et al. 2016; Musielak et al. 2019). Conversely, GO possesses several limitations including (1) great affinity of aggregation that declines the efficiency of adsorption capability (Petosa et al. 2010), (2) very challenging to disperse in the medium (Yang et al. 2017), and (3) difficulties in recycling of GO from treated solvent during toxic substances encapsulation process (Banerjee et al. 2015). Hence, these weaknesses can be solved by preparing composite hydrogels, in which GO nanoparticles are impregnated in the matrixes of polymer hydrogels (Abolhassani et al. 2017; Chang et al. 2014). In hydrogel matrices, GO acts as a reinforcing stimulus, consequently the properties of hybrid hydrogels were improved markedly. Also, polymer network prevents the agglomeration of GO nanoparticles and lessens fouling tendency in separation processes. The hybrid hydrogels containing GO are typically prepared by physical crosslinking methods. This method reduces threats associated with the toxicity of hydrogels because chemical crosslinkers were not used for the preparation of hybrid hydrogels (Crini and Lichtfouse 2019). For example, GO hybrid hydrogels were prepared by dispersion of GO into the anionic polymeric network, which has high adsorption capacities for elimination of cationic organic dyestuffs (Zhuang et al. 2016). The dye removal efficiencies of carbon nanomaterials hybrid hydrogels are tabulated in Table 16.1. Currently, Vo et al. (2020) designed chitosan/GO composite hydrogel by using ecofriendly chitosan and GO and studied the adsorption efficiency for remediation of both cationic and anionic dyes. These composite exhibited noticeable encapsulation capacities for removal of Methylene blue (MB), Rhodamine B (RhB), Methyl orange (MO), Congo red (CR) dyes. Additionally, the composite hydrogel can be easily reused after successive adsorption–desorption cycles. Chang et al. (2020) prepared chitosan/polyacrylate (pAA)/GO hybrid hydrogel for remediation of MB and food yellow 3 (FY3) dyes. In the hydrogel network, pAA markedly enhanced the swelling and adsorption capacity of hydrogel. In addition, GO acts as reinforcement agent, which improved both the adsorption and mechanical strength of hydrogels. The experimental findings showed that the hybrid hydrogel instantaneously adsorbed both MB and FY3 dyes having maximum uptake capabilities of 296.5 ± 31.7 mg $g^{-1}$ and 280.3 ± 23.9 mg $g^{-1}$, respectively. Dai et al. (2018) fabricated environmental friendly composite hydrogels, polyvinyl alcohol (pVA)/carboxymethyl cellulose (pCMC)/graphene oxide (GO)/bentonite, which is crosslinked physically and evaluated the adsorptive removal of MB dye. Their experimental results revealed that after incorporation of GO and bentonite into the hydrogels, reinforced the thermal stability, swelling capacity, and the dye uptake ability of hydrogels. The monolayer MB uptake capability of composite hydrogel was 172.14 mg $g^{-1}$, which is obtained from the Langmuir isotherm model. In addition, in absence of GO and bentonite in hydrogels, MB dye uptake capacity was only 83.33 mg $g^{-1}$. Also, the hydrogels exhibited good pH sensitivity and have

**Table 16.1** Adsorption capacity of carbon nanomaterial hybridized hydrogel adsorbents determined by Langmuir model for remediation of organic dye

| Organic dyes | Carbon nanomaterial hybridized hydrogel adsorbents | Adsorption capacity, $Q_{\max}$ (mg $g^{-1}$) | References |
|---|---|---|---|
| MB | CS/pAAc/GO | 297 | Chang et al. (2020) |
| MB | CS/GO | 390 | Chen et al. (2013) |
| CR | CS/GO | 10 | Zhao et al. (2015) |
| MB | CMC/pVA/GO | 89 | Dai et al. (2018) |
| MB | pEI/GO | 334 | Guo et al. (2015) |
| RhB | pEI/GO | 132 | Guo et al. (2015) |
| MB | CE/GO | 123 | Soleimani et al. (2018) |
| RhB | CE/GO | 62 | Soleimani et al. (2018) |
| MB | ALG/GO | 122 | Balkiz et al. (2018) |
| MB | Single ALG/GO network | 1840 | Zhuang et al. (2016) |
| MB | Double ALG/GO network | 2300 | Zhuang et al. (2016) |
| MB | Single ALG-PVA-GO network | 1256 | Kong et al. (2019) |
| MB | Double ALG/PVA/GO network | 1437 | Kong et al. (2019) |
| MB | ALG/MWCNTs | 14 | Li et al. (2012) |
| MB | pMAc-g-HE/MWCNTs | 222 | Sun et al. (2014) |
| CR | CS/CNT | 450 | Chatterjee et al. (2010) |
| MB | TG/CFCNT HBNC | 1092 | Mallakpour and Tabesh (2021) |
| MB | SA/pAAc/o-MWCNTs HNC | 1596 | Makhado et al. (2021) |

Abbreviations: *AAc* Acrylic acid, *ALG* Alginate, *SA* Sodium Alginate, *CE* Cellulose, *CMC* Carboxymethyl cellulose, *CS* Chitosan, *CFCNT* Carboxyl-functionalized carbon nanotube, *EI* Ethyleneimine, *VPA* Vinyl alcohol, *MAA* Methacrylic acid, *HE* Hemicellulose, *GO* Graphene oxide, *MWCNTs* Multiwall carbon nanotubes, *TG* Tragacanth gum, *HBNC* Hydrogel bionanocomposite, *o-MWCNTs* Oxidized multiwalled carbon nanotubes, *HNC* Hydrogel nanocomposite
Organic Dyes: *MB* Methylene blue, *CR* Congo red, *RhB* Rhodamine 6G

regeneration capacity for elimination of MB. Chen et al. (2013) fabricated physically crosslinked hydrogels, graphene oxide-chitosan (GO-CS) and studied the dye remediation of hydrogels for both cationic and anionic dyes. The experimental data showed the uptake capacities of hydrogels were 89 mg $g^{-1}$ and 390 mg $g^{-1}$ for anionic and cationic dye, respectively. In addition, adsorption mechanism was governed by the electrostatic interactions between composite hydrogel and dye molecules. Guo et al. (2015) facilely designed hybrid hydrogels using polyethyleneimine (pEI) and grapheme oxide (GO) and evaluated the adsorption capacity for remediation of MB and RhB dyes. The composite hydrogel showed superior dye encapsulation ability, which can be varied through the amount of pEI and GO. The findings data revealed that the encapsulation capacity of MB and RhB dyes onto hybrid hydrogels is 334 mg $g^{-1}$ and 132 mg $g^{-1}$, respectively. Conversely, the hybrid hydrogels, chitosan-GO, and cellulose-GO showed better adsorption efficiency towards cationic MB dye compared to RhB dye (Table 16.1). According to Kong et al. (2019), the single and double network hydrogel beads of calcium alginate and polyvinyl alcohol displayed very high adsorption capacities for remediation of MB dye from water. The maximal encapsulation capacities of single and double network hydrogel breads were 1256 mg $g^{-1}$ and 1437 mg $g^{-1}$, respectively, which determined from the Langmuir monolayer adsorption isotherm model. In addition, both hydrogels have remarkable regeneration capacity. On the other side, single network alginate-GO composite hydrogel showed very high uptake capacity of 1840 mg $g^{-1}$ and double network alginate-GO composite hydrogel showed $Q_{max}$ value of 2300 mg $g^{-1}$ for MB dye adsorption. Moreover, double network hydrogel bead has more recyclability compared to single network hydrogel and both hydrogels beads have NaCl tolerance ability.

Carbon nanotubes (CNTs) are composed of cylindrical molecules, which contain single layer rolled up graphene sheets (Sarkar et al. 2018; Vashist et al. 2018). According to the number of layers, CNTs are two types: (1) single-walled (SWCNTs), which comprise single layers graphene sheets with a diameter less than 1 nanometer (nm) and (2) multi-walled (MWCNTs) consist of several layers of concentrically interconnected nanotubes having a distance between two layer of approximately 0.34 nm and diameters are approximately 100 nm (Dai 2002; Aqel et al. 2012; Das et al. 2014; Postnov et al. 2016; Thakur et al. 2016). Lately, MWCNTs received considerable interests for organic dye remediation from effluent water owing to unique properties such as distinctive hollow tubular structure, large specific surface area, highly selective, structural diversity, and also favorable physicochemical stability. Moreover, MWCNTs are more attractive and cheaper carbonaceous materials compared to SWCNTs (Santhosh et al. 2016). To date, MWCNTs have received special interest as one of the most promising nanomaterials into the polymer network for enrichment thermal and mechanical properties (Ma et al. 2012). Generally, MWCNTs hybrid hydrogel was synthesized by integration of MWCNTs into the polymer hydrogel networks. The combination of MWCNTs nanomaterials in hydrogel networks can improve the performance of hybrid hydrogels. But the lack of reactive functional units on the surfaces of nanotubes sometimes limits their utilization for dye removal process. Thus, it is necessary to treat the MWCNTs before use, by incorporation of polar reactive moieties on the surfaces of MWCNTs (Ma et al. 2012). Indeed, some researchers used pre-treated MWCNTs for fabrication of the MWCNTs hybrid hydrogels and investigated it for adsorptive removal of organic dyes. For instance, chitosan-based MWCNTs hybrid hydrogel beads have been evaluated for elimination of CR dye (Chatterjee et al. 2010). This study revealed that the unification of MWCNTs onto the hydrogel matrixes enhanced the thermal stability, mechanical strength, and dye removal capacity. Table 16.1 shows the maximum adsorption capacity of different carbon nanomaterials hybrid hydrogels for organic dye remediation. Makhado and coworkers prepared composite hydrogels based on copolymer of acrylic acid (AA) onto xanthan gum (XG) and oxidized MWCNTs and investigated the adsorption behavior of MB dye from water. The experiment outcomes indicated that the hydrogel exhibited very fast adsorption rate and have excellent regeneration ability (Makhado et al. 2018). Very recently, Mallakpour and Tabesh (2021) prepared biocompatible Tragacanth gum (TG)-carboxyl-functionalized carbon nanotube (CFCNT)-hydrogel bionanocomposite (HBNC) for MB dye adsorption process and determined that the removal efficiency was 80% under optimum conditions and the maximum adsorption capacity of nonlinear and linear Langmuir model is 1092 and 647 mg/g, respectively. Makhado and Hato (2021) prepared sodium alginate (SA)/poly (acrylic acid) (pAAc)/oxidized-multiwalled carbon nanotubes (o-MWCNTs) hybrid hydrogel by using graft copolymerization method. The obtained composited hydrogels were used for remediation of MB blue dye from effluents water. Their findings revealed that the composite hydrogels exhibit very high adsorption capacity ($Q_{\max}$ = 1596.0 mg $g^{-1}$) under optimum experimental condition. In addition, the hydrogels have very good recyclability.

## 16.3 Silica Nanoparticle-Hybridized Hydrogels for Remediation of Organic Dye

Silica nanoparticles (Si) are one of the versatile materials, which can be utilized in several applications including contact lenses, imaging, biomedical fields, and adsorption of toxic substances. Si has many advantages such as high surface area, thermal stability, functionalizable and tuneable particle size. The surface of silica can be easily functionalized with vinyl group via grafting method using organic ligands, which further formed covalent bond with macromolecules or making multifunctional and steady hybrid materials. Specifically, silica hybridized hydrogels are considered to be one of the most attractive substances because of its easy availability, small fabrication cost, high adsorption capacity, excellent regeneration ability, selectivity, and ecofriendly (Rahman et al. 2021b; Soares et al. 2017: Thirumavalavan et al. 2011; Singh et al. 2009). However, the major drawback of polymeric hydrogels is poor mechanical strength, which hindered hydrogels in different applications. Hence, to enhance the mechanical strength of hydrogels without altering the important properties is a key concern in designing hybrid hydrogels. So, the combination of Si onto the hybrid hydrogel networks is possibly an ideal method and Si could be firmly bound with the polymeric matrixes, resulting in increased mechanical strength of Si hybrid hydrogels. Because of this benefit, silica-based hybrid hydrogels have been extensively considered for adsorption of toxic substances from water. However, in the last few decades, extensive research has been done to the modification of inorganic Si with different natural and synthetic polymers using various approaches. Based on the fabrication method, morphological features, size and size distribution, and chemical composition, the modified Si particles are considered to have different properties. However, Si hybridized hydrogels were generally prepared in situ sol-gel process, which is considered as an attractive technique for homogeneous distribution of nanoparticles within the polymer network and hence enhanced the strength of hybrid hydrogels. It is well-known that the sol-gel reaction comprises the hydrolysis of nanoparticles precursors and condensation of the subsequent hydroxyl groups to formation of a network structure that hinder aggregation of nanoparticles and increase homogeneous dispersion of nanoparticles. Therefore, in situ sol-gel technique for formation of nanoparticles in hydrogel could effectively increase the compatibility and as a result boosted the mechanical properties. Xie and coworkers utilized silane-coupling agent including vinyltriethoxysilane (VTES), tetraethyl orthosilicate (TEOS), and γ-methacryloxyp ropyltrimethoxysilane (MPTMS) as Si precursors, and they obtained uniform Si through sol-gel process. The in situ sol-gel polymerization process has some drawbacks including the purification of hydrogels requires a long time and sometimes unreacted monomer or initiator to remain in the hydrogel network, which has a detrimental effect in some applications specifically in biomedical applications. Conversely, direct mixing of previously prepared copolymer containing reactive side chain (trimethoxy silly group) and Si was regarded as a more efficient technique for preparation of Si hybrid hydrogel (Takafuji et al. 2011). In this Si hybrid hydrogel hydroxyl group of Si reacted with trimethoxysilyl side chains, which resulted in formation of three-dimensional crosslinked networks where Si distributed more homogeneously in the hydrogel matrixes. Moreover, covalent binding of Si with reactive side chain of copolymer also improves the compatibility and the strength of Si hybrid hydrogel. Furthermore, this method also has some advantages compared to in situ sol-gel polymerization methods such as highly transparent and homogeneous network structure, free of unreacted monomer and initiator, and simple preparation method. Moreover, the swelling and deswelling capacities of hydrogels feasibly adjusted simply via altering the compositions of Si and reactive copolymer (Rahman et al. 2021a, b). Figure 16.2 shows some typical examples of silica crosslinked hybrid hydrogels. Takakafuji and coworkers reported a unique strategy for fabrication of Si crosslinked co-polymeric hybrid hydrogels using a hydrophilic copolymer having trimethoxysily groups as reactive side chain, in which Si acts as a multiple cross linker (Takafuji et al. 2011). Based on this strategy, very recently, Rahman and coworkers fabricated the acrylamide hybrid hydrogels using reactive copolymer, poly (*N*-(3-methoxy propyl acrylamide-co-3-methacryloxypropyl trimethoxysilane) (*p*MS) or poly (acrylamide-co-3-methacryloxypropyl trimethoxysilane) (*p*AS) with silica nanoparticles (Si) and applied these hybrid hydrogels for efficient encapsulation of MB dye from water. Their findings revealed that the Si crosslinked acrylamide hybrid hydrogels have very high adsorption capacities compared to other silica-based hybrid hydrogels. The obtained adsorption capabilities of *p*MS-Si and *p*AS-Si hydrogels were 588.23 and 666.65 mg $g^{-1}$, respectively, for MB dye adsorption under optimum conditions. In addition, the hydrogels showed high recycling ability and also highly selective towards the MB in a binary dye solution (Rahman et al. 2021a, b).

Recently, Xu and coworkers prepared a dual nanocomposite hydrogel having dual properties by clay nanosheets, for instance, Laponite or bentonite and also used different inorganic materials including graphene oxide (GO), silica nanoparticles (Si), and titanium oxide (Ti) as a crosslinking agent. Therefore, the mechanical

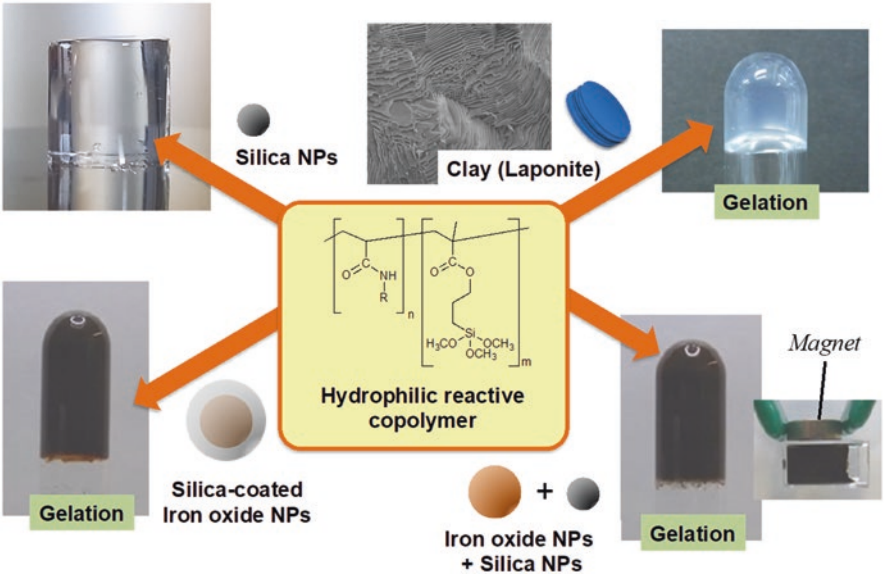

**Fig. 16.2** Typical hybrid hydrogels composed of nanoparticle crosslinked reactive copolymer network

strength of resulting hydrogels was enhanced markedly. Generally, Si was obtained from MPTMS, TEOS, VTES and Ti was obtained from tetrabutyl titanate (TBOT) by universal sol-gel technique. After that hybrid hydrogels were prepared via simultaneous sol-gel and free-radical polymerization technique. An important factor on enriched mechanical properties is that the GO, Si, or Ti acted as multifunctional crosslinkers via assembly with clay nanosheets during the polymerization process. In addition, the covalent bond is made between clay nanolayers and GO, Si, or Ti during in situ sol–gel process. Subsequently, the compatibility of nanoparticles with polymer matrix was improved greatly. Also, the strength of the dual nanocomposite hydrogel was markedly increased, which was more efficient than hydrogel prepared by any of the two nanoparticles. Ghorai et al. (2014) prepared hybrid hydrogel composed of hydrolyzed polyacrylamide (pAM) grafted onto xanthan gum (XG) and silica nanoparticles ($SiO_2$). They used the composite materials for encapsulation of MB and MV dyes and obtained very high removal efficiency of (XG-g-pAM / $SiO_2$) for both dyes. The experimental results revealed the maximal adsorption efficiencies of 497.5 mg $g^{-1}$ and 378.8 mg $g^{-1}$, respectively, for MB and MV dye removal onto (XG-g-pAM/$SiO_2$) hydrogel. Also, the hybrid hydrogel has excellent regeneration ability and hence considered as a promising adsorptive material for remediation of toxic dyestuffs from effluents water. Pal and their coworkers synthesized polyacrylamide grafted carboxymethyl tamarind (CMT-g-pAM)/$SiO_2$ nanocomposites for remediation of MB dye from an aqueous solution. The nanocomposite hydrogel displayed the highest adsorption capacity of 43.85 mg $g^{-1}$ and also has good regeneration capacity (Pal et al. 2012). The encapsulation capacities of different silica-based hybrid hydrogels for remediation of dyestuffs from water are presented in Table 16.2.

To date, Chen and coworkers reported vinyl hybrid silica nanoparticles (VSNPs) based super-adsorbent nanocomposite (NC) hydrogel. The fabricated NC hydrogel adsorbents accomplished excellent MB dye encapsulation capacity of 1690 mg/g and also 90% of MB removal was achieved in 40 min. Moreover, the NC hydrogel showed outstanding regeneration capacity (Chen et al. 2021). In another study, Si comprising xanthan gum-graft-polyacrylamide hybrid hydrogel exhibited good adsorption capacity towards both MB and MV dyes (Ghorai et al. 2014).

Hosseinzadeh and coauthors synthesized nanocomposite hydrogel adsorbent using sodium alginate and silicone dioxide nanoparticles by free-radical graft copolymerization method and the nanocomposite hydrogel was utilized for MB dye removal process. The experimental results indicated that the hydrogel has pH-responsive behavior, thus studied the swelling–deswelling properties at pH 2.0 and 9. Thus, adsorption properties depended on the synergistic effect and the specific surface area of $SiO_2$ nanoparticle distributed in the hydrogel network. The hydrogel

**Table 16.2** Adsorption capacity of silica nanomaterial hybridized hydrogel adsorbents determined by Langmuir model for remediation of organic dye

| Organic dyes | Hydrogels | Adsorption capacity, $Q_{max}$ (mg $g^{-1}$) | References |
|---|---|---|---|
| MB | CMT-g-pAM/$SiO_2$ | 43.8 | Pal et al. (2012) |
| MB | $SiO_2$-g-pAA | 375.9 | Saleh et al. (2020) |
| MB | VSNPs/pAAc-AM) | 1670 | Chen et al. (2021) |
| MB | *p*MS-Si | 588.23 | Rahman et al. (2021a, b) |
| MB | *p*AS-Si | 666.65 | Rahman et al. (2021a, b) |
| MB | NaAlg/$SiO_2$ | 148.23 | Hosseinzadeh and Abdi (2017) |
| MB | *p*(MAA-co-MMA)/$SiO_2$ | 85.3 | Jamwal et al. (2017) |
| MB | (MAA-*co*-HPMA)/$SiO_2$ | 87.3 | Jamwal et al. (2017) |
| MB | pAAc/$SiO_2$ | 400.0 | Zulfikar et al. (2020) |
| MB | (PAA/$SiO_2$/TMPTMS) | 437.7 | Zulfikar et al. (2020) |
|  | (pAM-co-DADMAC)/ silica sol | 31.3 | Yang et al. (2015) |
| MB | XG-g-pAM/$SiO_2$ | 497.5 | Ghorai et al. (2014) |
| MV | XG-g-pAM/$SiO_2$ | 378.8 | Ghorai et al. (2014) |
| MB | GK-cl-p(AA-co-AAM)/ $SiO_2$ | 1408.67 | Mittal et al. (2015) |

Abbreviations: *AM* Acrylamide, *AA* Acrylic acrylamide, *AAc* Acrylic acid, *CMT* Carboxy methyl tamarind, *DADMAC* Diallyl dimethyl ammonium chloride, *HPMA* 2-hydroxypropyl methacrylate, *TMPTMS* 3-Mercaptopropyltrimethoxylane, *MAA* Methacrylic acid, *MMA* Methyl methacrylate, *pAS* poly(acrylamide-co-3-methacryloxypropyl trimethoxysilane), *pMS* (*N*-(3-methoxy propyl acrylamide-co-3-methacryloxypropyl trimethoxysilane), *NaAlg* Sodium alginate, *VSNPs* Vinyl hybrid silica nanospheres, XG Xanthan Gum, *GK* Gum karaya
Organic Dyes: *MB* Methylene Blue, *MV* Methyl Violet

exhibited high MB removal efficiency, recyclability, and highly selective toward cationic dye (Hosseinzadeh and Abdi 2017). Blachnio et al. (2018) synthesized chitosan-silica composites having different surface and structure properties. These hybrid hydrogels, compose of silica nanoparticles that play an important role for adsorption rate and capacity of anionic azo dye. Soares et al. (2017) prepared magnetic hybrid hydrogels using κ-carrageenan, saline coupling agents TEOS as silica source and $Fe_2O_3$ via sol-gel process and investigated it for MB dye adsorption. The findings showed the magnetic hybrid hydrogel has high dye removal rate and the maximum uptake ability of MB dye was 530 mg $g^{-1}$. It might be facilely regenerated by washing through potassium chloride aqueous solution and the dye elimination efficacy was over 97% after six adsorption–desorption cycles. In another study, Mittal and coworkers synthesized hydrogel nanocomposite using Gum kara grafted onto poly (acrylic acid-acrylamide) (GK-cl-p (AA-*co*-AAM)) and $SiO_2$ nanoparticle-hybridized (GK-cl-p (AA-*co*-AAM)) hydrogels were prepared via hydrolysis of TEOS, which is dispersed in polymer hydrogel. The hybrid hydrogel was used for adsorptive remediation of MB dye. According to their experimental results, the adsorption process best fit with the Langmuir monolayer isotherm model with highest adsorption capacity of Langmuir 1408.67 mg $g^{-1}$ that was very high compared to polymer hydrogel only. Additionally, (GK-cl-p (AA-*co*-AAM)) hydrogel exhibited excellent recyclability in acidic medium and the adsorption efficiency reduced after three repeated cycles (Mittal et al. (2015)).

## 16.4 Metal and Metal Oxide Nanoparticle-Hybridized Hydrogels for Elimination of Toxic Dye

Nowadays various metal and metal oxides (MOs) including silver (Ag), gold (Au), copper, zinc oxide (ZnO), copper oxide (CuO), titanium dioxide ($TiO_2$), and iron oxide ($Fe_2O_3$, $Fe_3O_4$) nanoparticles are one of the most promising materials for dye encapsulation processes owing to their distinctive characteristics, including large surface area, very high reactivity, amendable size and shape, thermal and electrical conductivity, magnetic properties, and strong solution mobility (Wang et al. 2020a, b). Therefore, various metal and MOs nanoparticles were incorporated onto the hydrogel networks for fabrication of novel nanomaterial hybridized composite hydrogels. In these hydrogels, MOs nanoparticles markedly enhance the properties of hydrogels and also afford the catalytic activity in deterioration of organic contaminants. In addition, MOs play important role to tuning the swelling and adsorption–desorption of hydrogels through regulating the exterior magnetic field in case of MO having assessable magnetic properties (Abdullah et al. 2019). However, metal and MOs nanoparticles sometimes oxidized in acidic conditions, which sometimes cause secondary pollution owing to the leaching of MOs from composite. This problem can be addressed by using capping agents such as silane-coupling agents, polymeric hydrogel network, and so on. In addition, MOs in polymer matrixes prevent the agglomeration of MOs nanoparticles resulting in increased reactive surface areas (Facchi et al. 2018; Nakhjiri et al. 2019). There are several methods to incorporate the MOs nanoparticles onto the polymer hydrogel matrixes, which included: (1) simply adding the MOs into pre-prepared hydrogel, (2) just mixing the MOs in situ gelation process, and (3) by entrapped during the swelling process. However, these methods have some drawbacks that the metal and MOs nanoparticles are embedded physically into polymeric matrixes of hydrogel. Therefore, consistent discharge of nanoparticles from the hydrogel matrixes into the external atmosphere may cause detrimental effects in the environment. To solve this issue, a new synthesis technique is used to fabricate the hybrid hydrogels containing functionalized MOs nanoparticles that are covalently bonded with the polymer networks. To prepare the covalent bonded MOs hybrid hydrogel, at first, MOs were surface functionalized through amine groups via coating them with (3-aminopropyl)-trimethoxysilane (APTMS) (Pasqui et al., 2011). Therefore, amidic bonds formed between the $-NH_2$ groups of MOs surfaces and the functional group of polymer, resulting in three-dimensional networks formed. The uniqueness of this technique is that the MOs nanoparticles act as crosslinkers for fabrication of hybrid hydrogel. Thus, the hybridized hydrogel obtained has enhanced properties including mechanical, swelling, optical, and catalytic properties. In the two last decades, MOs hybrid hydrogels have extensively been used in toxic substance remediation from water owing to the outstanding properties, for instance, high reactivity and specific surface area and also ability to regeneration of hydrogels efficiently after adsorption processes. In view of this, several MOs hybrid hydrogels used for remediation of toxic organic dyestuffs are summarized in this section. Among the MOs, magnetic nanoparticles hybrid hydrogels have been most fascinating materials for remediation of organic dyestuffs owing to the non-toxic nature, cost-effective, and high efficiency (Ahmadi et al. 2014). In addition, this hybrid hydrogel can easily be regenerated from solution by magnetic attraction (Zhang et al. 2016; Zhao et al. 2016). This property made magnetic hybrid hydrogel more efficient and economic compared to other MOs hybrid hydrogels.

Song et al. (2018) prepared hyperbranched polyglycerol embedded with decorated $Fe_3O_4$ nanoparticles magnetic hydrogel via smart thiol-ene click chemistry method and used the hydrogels for remediation of MB and MV dyes (Table 16.3). They showed that the hydrogels have fast adsorption rate and high adsorption capacity ($Q_{\max} = 458.7$ for MB and $Q_{\max} = 400.0$ mg g$^{-1}$ for MV). In addition, the magnetic hydrogels were highly selective towards cationic dye. Moreover, this hydrogel has magnetic separation characteristic and the regenerated hydrogel can be reused for several cycles without decline its efficiency. In another study, magnetic nanoparticles hydrogel composite was prepared by incorporating iron oxide onto chitosan–graphene oxide matrixes, and applied this nanocomposite hydrogel for MB dye removal. The results showed the hydrogel has an excellent MB removal adsorptive property and regeneration capacity. This adsorption property of MOs hybrid hydrogel can be influenced by the nature of MOs and the amount of MOs in the hydrogels. For instance, addition of excess MOs in the hydrogels can increase the

**Table 16.3** Adsorption capacity of different metal oxides hybridized hydrogels and nanomaterial-hybridized polysaccharide hydrogel adsorbents for remediation of organic dyes

| Organic dye pollutant | Metal hybridized hydrogel adsorbents | Adsorption capacity, $Q_{max}$ (mg g$^{-1}$) | References |
|---|---|---|---|
| AB | CS/$Fe_3O_4$ | 142 | Xu et al. (2019) |
| MB | HPG/$Fe_3O_4$ | 459 | Song et al. (2018) |
| CR | PAAm-*co*-AAc/$TiO_2$ | 2.2 | Kangwansupamonkon et al. (2018) |
| CV | PAAm/$TiO_2$ | 132 | Raj et al. (2018) |
| MB | PAAc/$Co_3O_4$ | 837 | Ansari et al. (2019) |
| MB | PVPA/$Fe_3O_4$@$SiO_2$ | 14 | Sengel and Sahiner (2016) |
| MB | AMPS/NIPAAm/$Fe_3O_4$ | 833 | Atta et al. (2018) |
| MB | AMPS/NIPAAm/$Cu_2O$ | 341 | Atta et al. (2018) |
| MB | AMPS/ NIPAAm /$Fe_3O_4$.$Cu_2O$ | 746 | Atta et al. (2018) |
| MG | PAAc-*co* AAm/$Co_3O_4$.$Cu_2O$ | 238 | Naseer et al. (2018) |
| MV | HPG@ $Fe_2O_3$ | 400 | Song et al. (2018) |
| MB | SA-pAA/ZnO | 1529.6 | Makhado et al. (2020) |
| RhB | PVPA/$Fe_3O_4$@$SiO_2$ | 16 | Sengel et al. (2016) |
| RhB | PMOA/ATP/$Fe_3O_4$ | 1.7 | Yuan et al. (2015) |
| MB | ALG/AgNPs | 214 | Devi et al. (2016) |
| MV | PAAc-*g*-ALG/$TiO_2$ | 1157 | Thakur and Arotiba (2018) |
| RhB | PAAc-*g*-salep/AgNPs | 93 | Bardajee et al. (2016) |
| MB | CE/κ-CARR/$TiO_2$ | 115 | Jo et al. (2017) |
| AAB | ALG@yttrium | 1087 | Liu et al. (2020) |
| AB | CS@$Fe_3O_4$ | 142 | Xu et al. (2019) |
| MB | CMC/PVA/GO | 172.4 | Dai et al. (2018) |
| MB | (CMC-cl-pAA/$Fe_3O_4$-C30B) | 1081 | Malatji et al. (2020) |
| MB | CMC/$Fe_3O_4$@Si | 620 | Uva et al. (2017) |
| MB | MCNCs/starch-g-(AMPS-co-AA) | 2500 | Moharrami and Motamedi (2020) |
| MB | CMS/PVA/$Fe_3O_4$ | 23.5 | Gong et al. (2015) |
| MB | CS/CMC/GO | 122.2 | Kaur and Jindal (2019) |
| MB | PAAm/CS/$Fe_3O_4$ | 1603 | Zhang et al. (2020) |
| MB | CS/GO/$Fe_3O_4$ | 74.9 | Singh et al. 2019 |
| MB | CS/PAA/ MMT/$TiO_2$ | 294.4 | Wang et al. (2019) |
| MB | SA/PVA/$Fe_3O_4$ | 781.9 | Niu et al. (2021) |
| MB | SA/PAAc/ZnO | 1529.6 | Makhado et al. (2020) |

Abbreviations

*AAC* Acrylic acid, *AAm* Acrylamide, *ALG* Alginate, *AMPS* 2-acrylamido-2-methyl-1-propanesulfonic acid, *CE* Cellulose, *CMC* Carboxymethyl cellulose, *CS* Chitosan, *CMS* Carboxymethyl starch, κ-*CARR kappa*-Carrageenan, *GO* Graphene oxide, *HPG* Hyperbranched poly glycerol, *NIPAAm* n-isopropyl acrylamide, *SA* Sodium alginate, *PMOA* Poly(2-(2-methoxyethoxy) ethyl methacrylate-*co*-oligo(ethylene glycol) methacrylate-*co*-acrylic acid), *PVA* Poly(vinyl alcohol, *pVPA* poly(vinyl phosphonic acid), *MMT* montmorillonite, *MCNCs* magnetite-functionalized cellulose nanocrystals

Nanomaterials: $Co_3O_4$ Cobalt(III) oxide, $Cu_2O$ Copper (I) oxide, $Fe_2O_3$ Iron (III) oxide, $SiO_2$ Silica nanoparticles, $TiO_2$ Titanium oxide, *ZnO* Zinc oxide

Dyes: *AB* Acid blue, *AAB* Acid brilliant blue, *CR* Congo red, *CV* Crystal violet, *MB* Methylene Blue, *MG* Malachite green, *MV* Methyl violet, *RhB* Rhodamine 6G crosslinking density of hydrogels, resulting in decline in the swellability and also dye adsorption capacity. Hence, the amount of MOs should be optimized into the hydrogel networks to achieve high dye efficiency of hybrid hydrogel (Singh et al. 2019). Dai et al. (2019) designed pineapple peel cellulose/magnetic diatomite hydrogels for MB dye removal. They noted the amount of dye removal capacity of hydrogel varied based on the magnetic $Fe_3O_4$-diatomite dose. According to their experimental results, highest amount of MB dye removal was achieved at low $Fe_3O_4$-diatomite dose (200 mg) and the adsorption capacity was declined at higher $Fe_3O_4$-diatomite dose (600 mg) compared to pineapple peel cellulose. Even though the composite hydrogel seems to be more efficient for dye removal, on the other side, the fabrication of this hydrogel still has some challenges including aggregation of MOs nanoparticles affecting appropriate dispersion of nanoparticles, which reduces the reactive surface area of MOs in the hydrogel matrixes. Also, phase separation occurs sometime that reduces the interaction between hydrogel and MOs nanoparticles (Li et al. 2013). However, very recently photosensitive metallic compounds including $TiO_2$, ZnO, CuS, and $MoS_2$ have been used for designing composite hydrogels. These photovoltaic material-based hydrogels are highly promising materials owing to both degradation and adsorption of dyestuffs, which occur instantaneously. For instance, Chen et al. (2017) designed hydroxypropyl cellulose/$MoS_2$ composite hydrogel for MB dye removal. Experimental results showed that the composite hydrogel showed higher adsorption efficiency compared to hydroxypropyl cellulose hydrogel, which was prepared conventionally in the same experimental condition owing to the presence of $MoS_2$ particles into the hydrogel matrixes. Moreover, the hydrogel can be photo-regenerated easily using sunlight without loss of MB absorption efficiency of hydrogels. So the composite hydrogels having both adsorption and photo-degradation capacity could be highly promising materials for toxic substances removal from water. On the other side, additional experiment should be conducted to detect the secondary product produced from photo-degradation. Very recently, Reza et al. (2017) noted the main demerits of oxidative degradation method as it produces toxic secondary byproducts. To date, ZnO nanoparticles (ZnO NPs) are also one of the prominent materials for toxic dye remediation process owing to its availability, biocompatibility, and cost-effectiveness (Amirmahani et al. 2020; Malakootian et al. 2019). In another study, hydrogel nanocomposite, sodium alginate-poly (acrylic acid)/zinc oxide (SA-pAAc/ZnO) was used for adsorptive remediation of MB dye from water and the obtained results were compared with the adsorption efficiency of sodium alginate-poly (acrylic acid) (SA-pAAc) hydrogel without ZnO nanoparticles. The results showed the maximum uptake of MB dye was 1129 mg/g and 1529.6 mg/g, respectively, for the SA-pAAc hydrogel and (SA-pAAc)/ZnO composite hydrogels in optimum condition within 40 min. Moreover, SA-pAAc/ZnO hydrogel exhibited outstanding regeneration ability compared to SA-pAA hydrogel (Makhado et al., 2017).

Tamer et al. (2018) prepared hybrid hydrogel using ZnO and alginate as a polymer template and investigated MB dye removal capacity. According to their strategy, Zn ions were utilized for ionic gelation of alginate and after that ZnO nanoparticles were prepared via calcination of the obtained gel at a suitable temperature. The experimental results indicated that MB dye removal was achieved within very short time. Vahidhabanuet et al. (2017) designed ZnO–clay–alginate beads hydrogel column for removal of CR dye from aqueous solution and found the highest dye uptake capacity of 546.89 mg/g and also the hydrogels beads can be efficiently reused several cycles.

Very recently, Mittal and coworkers fabricated hybrid hydrogel based on the ZnO nanoparticles incorporated Gum Arabic grafted polyacrylamide (GA-cl-PAM) hydrogel template and studied the adsorption properties hydrogel for elimination of MG dye from effluent water. According to their study, ZnO NPs into the hydrogel networks reinforce the properties of hydrogels, hence increase the dye encapsulation ability of hydrogels. In addition, the hybrid hydrogel can repeatedly be used several adsorption–desorption cycles (Mittal et al. 2020a, b). In another report, hybrid hydrogel of poly(acrylic acid)-silver/silver nanoparticles (PAAc-Ag/AgNPs) was used for adsorption of organic dye. The highest dye uptake capacities of CR, RhB, and MB were determined as 15.17, 4.52, 14.08 mg $g^{-1}$, respectively (Hou et al. 2016).

## 16.5 Nanomaterial's Hybridized Polysaccharide Hybrid Hydrogels for Organic Dye Removal

Polysaccharides have been widely used in several fields including effluent water remediation, biomedicine, and agriculture owing to their low-toxicity, cost-effective, large specific surface area, and environmentally safe (Fu et al. 2019; Thakur et al. 2018; Kabir et al. 2018). Nowadays, polysaccharides based adsorbents are considered as "green adsorbents" for toxic substances remediation from effluent water owing to low cost, ease of availability, non-toxic, biodegradability, and the possibility of modification with various functionalities. Polysaccharides are, generally, hydrophilic polymer having repeating subunits of sugar, which is connected through glycosidic bonds. The presence of numerous functional groups including hydroxyl (-OH), sulfonic acid (-$SO_3H$), carboxylic acid (-COOH), amino (-$NH_2$) and amide (-$CONH_2$) groups, which can act as binding sites of biomolecules. Consequently, these biomolecules are highly effective for removal of toxic dyestuffs from water (Mittal et al. 2016). However, natural polysaccharides, for example, cellulose, starch, chitosan, carrageenan, and xanthan gum are commercially accessible (Huang et al. 2019; Motamedi et al. 2020; Wang et al. 2019). The surface functionalities of polysaccharide can be altered by graft copolymerization and incorporation of precise nanoparticles. Nanoparticles, for instance, $Fe_2O_3$, $TiO_2$, $SiO_2$, and carbon nanomaterials onto polymeric supports have been utilized to advance the characteristics of hydrogels (Mohammed et al. 2015; Pereira et al. 2020). The engineering of nanoparticle in the hybrid hydrogels increases the physicochemical properties of hydrogels. In addition, this strategy avoids leaching of nanomaterial and organic substances. Among the polysaccharides, cellulose is the most abundant, low cost, biodegradable and renewable polymeric materials in nature. It has previously been used for preparation of physically crosslinked hydrogels and also utilized for water treatment applications. There are two types of water-insoluble cellulose available: (1) cellulose nanocrystals (CNCs) and (2) cellulose nanofibers (CNFs). Between two types of cellulose, CNCs are smaller size rod-like structures having diameter in nanometer scale and also different surface functionalities such as carboxylate and sulfate can be been incorporated into their crystalline surfaces, which is beneficial for creating them as electrostatic crosslinks. Similarly, CNFs have widths in nm scale as CNCs but the length is in μm-scale. In addition, different functionalities have also been added in CNFs, which act as polyions into the crosslinked networks. Both CNCs and CNFs are considered an excellent building blocks for strengthening polymeric hydrogel networks, because of their diameter in nm scale, extraordinary aspect ratio, and distinctive web-like structure (Xiao et al. 2017). Additionally, numerous hydroxyl (–OH) groups present on CNs surfaces, which enable incoming functional groups to be uniformly distributed onto the polymeric networks and also influence the formation of electrostatic and hydrogen-bonding interactions between functional groups of CNs and host polymeric networks (Yue et al. 2019).

Recently, CNCs are considered as one of the efficient nanoadsorbent materials for remediation of toxic substances from water. Also, it is also considered as one of the most prominent reinforcement agents for making nanocomposite hydrogels, which is feasible, biocompatible and having enhanced adsorption capacity and reusability (Shojaeiarani et al. 2019). However, CNCs were, generally, synthesized from enzymatic-mediated sugar-beet pulp (SBP) by acid hydrolysis. It is usually used for preparation of physically crosslinked hydrogel and the obtained hydrogel was applied for adsorptive removal of toxic organic dyes. Mohammed et al. (2015) describe the synthesis process of hydrogel beads using alginate and sulfated cellulose nanocrystals (S-CNCs) and used it for MB dye removal. According to their experimental results, the hydrogel beads efficiently eliminate 97% of MB from aqueous solution and the maximum monolayer adsorption capacity of 256.41 mg $g^{-1}$. In another study, Wang et al. (2018) illustrated carboxylated CNF aerogels for MB removal having up to 95% efficiency and the maximum MB removal efficiency of 127.73 mg $g^{-1}$. In both examples, prolonged batch times (> 30 min) are required to achieve high removal efficiencies; therefore, the modification of these materials is highly desirable for rapid adsorption of organic dye. The adsorption capacity, thermal stability, and mechanical strength of CMC and CS are reinforced by incorporating different nanomaterials including graphene oxide (GO), titanium oxide ($TiO_2$), zinc oxide (ZnO), silica nanoparticles ($SiO_2$), and iron oxide ($Fe_2O_3$). In addition, functionalization of cellulose has shown efficiency in the extension of applicability of cellulose nanoadsorbent for organic dyes.

Carboxy methylcellulose (CMC) and chitosan (CS) are also the most abundant linear polysaccharides and promising materials for wastewater treatment owing to the numerous functional groups in their structures. Incorporating different nanomaterials has reinforced the properties of CMC and CS. For instance, addition of GO sheets in CMC and CS in hydrogel network significantly improves the swelling property and selective adsorption capacity. The regeneration ability of the prepared nanocomposite was assessed through different adsorption–desorption cycles. The experimental results indicated that the GO reinforces the removal efficiency of composite hydrogels and also highly selective towards BG and MB dyes from effluents water. According to their experimental results, the highest MB dye uptake capacity was 620 mg $g^{-1}$. The adsorption process was influenced by the seawater owing to the seawater containing different ions and consequently declined the electrostatic force of interaction among the carboxylate groups onto the CMC and MB. Dai et al. (2018) prepared environmentally friendly hybrid hydrogel using polyvinyl alcohol and carboxymethyl cellulose hydrogels, which is strengthened by bentonite and GO. Then the hybrid hydrogel was investigated for adsorptive removal of MB dye. According to their experimental results, presence of GO and bentonite into the hydrogel networks markedly enriched the properties of hydrogel. Also, after incorporation of GO and bentonite into the hydrogel matrixes, MB dye uptake capacity of 172.14 mg $g^{-1}$ was obtained from the Langmuir isotherm model, which is more than that of hydrogels fabricated without adding GO (83.33 mg $g^{-1}$). Additionally, all the hydrogels exhibited noble regeneration ability; therefore, hydrogels synthesized using GO as reinforcement agent could be served as environmentally safe and an efficient adsorptive material for elimination of organic dyestuff from effluents water.

Alginate is another most common anionic polysaccharide, which is generally obtained from different types of brown algae. It is a linear polymer and composed of α-L-guluronic acid (G) and β-D-mannuronic acid (M). The properties of alginate mainly depend on the content of G and M units. In addition, G-units of alginate primarily act as intermolecular crosslinkers with different cations. However, nanomaterial-hybridized alginate hydrogels have attracted great consideration owing to the unique characteristics (Mittal et al. 2014). For instance, Thakur and coworkers designed a hybrid hydrogel using sodium alginate (SA), polyacrylic acid (pAAc), and $TiO_2$ via graft polymerization technique. In this hybrid hydrogel, $TiO_2$ acted as a reinforcement agent and plays important role for enhanced MB adsorption. The highest MB uptake capacity of $TiO_2$ reinforced hybrid hydrogel was 2257.36 mg $g^{-1}$. On the other side, absence of $TiO_2$ in hydrogel matrixes, MB removal capacity was reduced from 99.4% to 80% (Thakur et al. 2016). In another study, silica NPs ($SiO_2$ NPs) were used instead of $TiO_2$ NPs to design SA/pAAc/$SiO_2$ hybrid hydrogel and investigated the MB dye encapsulation capacity (Hosseinzadeh and Abdi 2017). The results showed MB encapsulation was relatively low in case of SA/pAAc/$SiO_2$ hydrogel owing to the less electronegative of $SiO_2$ NPs ($Q_{\max}$ = 148 mg $g^{-1}$) present into the hydrogel matrixes compared to $TiO_2$ NPs (Thakur et al. 2016). Makhado et al. (2020) prepared composite hydrogel (SA/pAAc/ZnO) and applied it for MB dye elimination. ZnO acts as a reinforcing agent into the hydrogel matrixes, which markedly improved the properties including swelling and mechanical of hybrid hydrogel. Therefore, MB dye removal rate was increased by using ZnO into hybrid hydrogel matrixes and obtained highest encapsulation capacity of MB was 1529.6 mg $g^{-1}$. The hybrid hydrogels have good recyclability and adsorption efficiency of hydrogel was slightly declined after four cycles. Likewise, Niu et al. (2021) prepared SA/PVA/$Fe_3O_4$@KHA magnetic hydrogel and applied it for removal of MB dye. The hybrid hydrogel efficiently removes MB in the presence of magnetic environment and achieved maximum dye encapsulation of 781.92 mg $g^{-1}$ and also exhibited excellent recyclability. Moreover, Zhang et al. (2020) designed hybrid hydrogel CS/PAAm/$Fe_3O_4$ magnetic hydrogel for MB dye adsorption. The hydrogels exhibited high adsorption efficiency and good regeneration ability. Similarly, Singh et al. (2019) fabricated CS/GO/$Fe_3O_4$ magnetic hydrogel using graphene oxide (GO) instead of PAAm. Thus, the hybrid hydrogel exhibited high thermal stability owing to the presence of GO (Singh et al. 2019). On the other side, the dye encapsulation rate reduced markedly compared to the magnetic hybrid hydrogel, CS/pAAm/$Fe_3O_4$. The reason behind is that the presence of more hydrophilic PAAm into the hydrogel matrixes plays important role for enhanced adsorption capacity of CS/PAAm/$Fe_3O_4$ compared to CS/GO/$Fe_3O_4$ magnetic hydrogel. Figure 16.3 shows the nanomaterial's hybrid polysaccharide hydrogels for MB dye removal from aqueous solution.

Carrageenan (CG) is a sulfated ($–OSO_3^-$) linear polysaccharide obtained from red seaweed. It is composed of disaccharide repeating units of galactose and anhydrogalactose units. It is anionic characteristic due to the presence of 15%–40% of ($–OSO_3^{-)}$ groups in their structure, which makes CG anionic characteristic (Liu et al. 2016). According to the number and position of sulfated groups in the galactose unit, CG is classified as three groups. Three major forms of carrageenan include kappa (*k*), iota (*i*), and lambda (*λ*). Among the CG, *λ and I can form gel physically, whereas* κ-CG is thermo and pH sensitive. κ-CG is widely used for preparation of hybrid hydrogel and the properties of κ-CG can be changed easily by crosslinking with oppositely charged ions. For instance, Yang et al. (2017) designed hybrid hydrogel using GO into κ-CG and used the materials for MB dye removal. The adsorption capacity (658.4 mg $g^{-1}$) was higher compared to the composite hydrogels chitosan (CS)/graphene oxide (GO) and carboxymethyl cellulose (CMC)/GO (Dai et al. 2018; Wang et al. 2020a, b; Vo et al. 2020; Kaur and Jindal 2019). In addition, incorporation of different nanomaterial's including inorganic metal oxides, silicates, and zeolites in the matrixes of hydrogel markedly enhanced the thermal, mechanical, and adsorption properties. Mittal et al. (2020a, b) fabricated κ-CG/PAAm/PMAA hydrogel using AQSOA-Z05 zeolite and used the hydrogels for MB dye remediation. According to their results, κ-CG/PAAm/PMAA hydrogel had excellent MB adsorption capacity (682.67 mg $g^{-1}$) in comparison with metal oxides and clay incorporated composite hydrogels. Currently, polysaccharide based hydrogel appeared to be gain huge attention among the researchers to remediation of toxic dyes from wastewater owing to their superior mechanical strength, high swelling ability, and regeneration ability. In addition, the incorporation of nanomaterials such

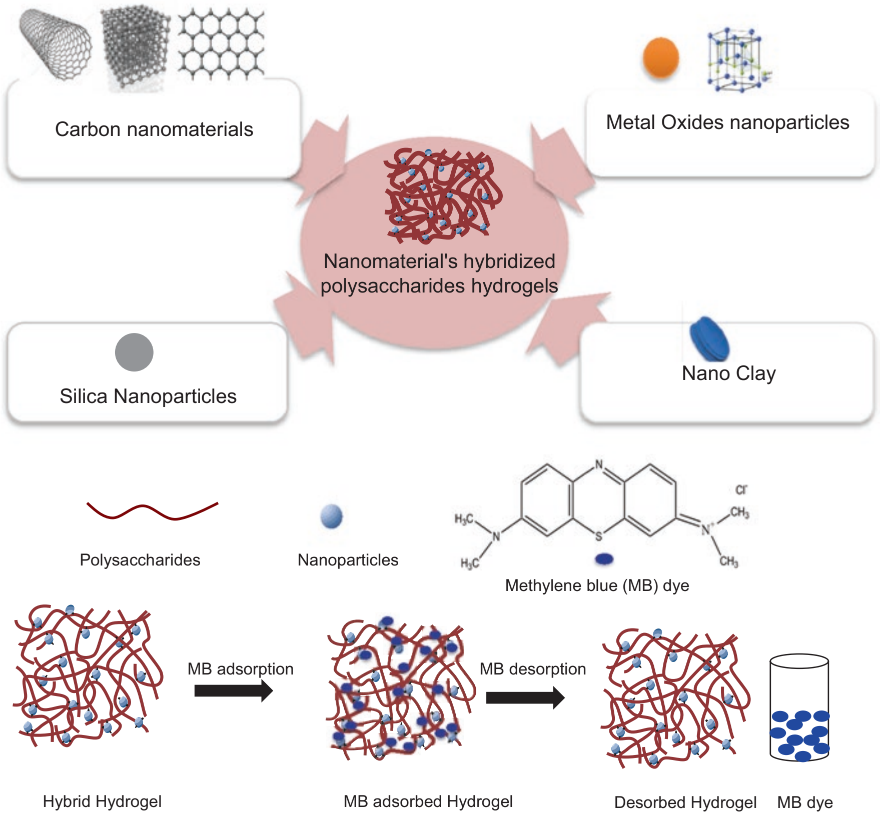

**Fig. 16.3** Schematic illustration of nanomaterial-hybridized polysaccharide hydrogels for dye removal from water

as MOs, rGO, and MWCNTs into the hydrogel network significantly increased hydrogel properties including mechanical properties and adsorption efficiency. The adsorption capacities of different polysaccharides are tabulated in Table 16.3. It is seen from table that sodium alginate composite hydrogels could be more efficient for MB dye encapsulation compared to the other polysaccharide hybrid based hydrogels.

## 16.6 Summary, Challenges, and Future Perspectives

In summary, the nanomaterial-hybridized hydrogels are promising materials for removal of organic dyes, which can retain the properties of both nanomaterial and hydrogel. The hydrophilic and interconnected micro-porous structures of the hydrogels appear to be spectacular materials for nanoparticles. Therefore, incorporation of these nanomaterial's into the hydrogel matrix improves the properties of hybrid hydrogels, which make them proficient for a specific application. However, in the last few decades, nanomaterials hybrid hydrogel absorbents have been used extensively for toxic substances removal from textile wastewater. This chapter demonstrated that hybrid hydrogels prepared from different polymers and nanomaterials, are benign, sustainable, and universal materials for treating organic dye contaminated water. Though, the high adsorption capacity and reusability make hydrogels very promising and interesting materials for remediation of textile dyes, there is still a need for further development of the hybrid hydrogels as an ideal adsorbent in view of some critical aspects. The following features and challenges need to mitigate for improvement of hybrid hydrogels: (1) enhancement of selectivity towards the specific dye and competent to remove coexistent contaminants both organic and inorganic ions, (2) upgrading of the reusability of the previously used hybrid hydrogels and enlargement of mechanical properties, which allow additional adsorption and desorption cycles, (3) investigation of encapsulation process using real industrial effluent water, (4) research and development of hybrid hydrogel columns to convert more cost-effective industrial and commercial products for large-scale application, and (5) understanding how the nanomaterial affects the intrinsic and adsorptive properties of resulting hybrid materials and also the deleterious effects of nanomaterials in the aquatic environments. Finally, if all shortcomings stated are rectified, nanomaterial's hybrid hydrogels are expected to be highly efficient adsorptive materials for large-scale removal of toxic substances from textile effluents water.

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# Chapter 17
# Legislative Policies and Industrial Responsibilities for Discharge of Wastewater in the Environment

**Shahenaz Jadeja and Shilpi Jain**

**Abstract** With the alarming water deficit around the globe, it is imperative to have policies that protect freshwater sources. Thus, removal of toxicants before discharge is of vital importance which may otherwise pose a threat to aquatic life and the surrounding environment. The growing demand for natural water supplies, as indicated by the effects of global climate change and shifting weather patterns, has sparked interest in reusing wastewater in recent years. Water resources management is the responsibility of government agencies, autonomous entities, industry, local government institutions, municipalities, and city corporations. The paradigm changed from seeing enormous amounts of wastewater as an expensive issue to seeing them as a useful resource. This has marked the beginning of building sustainable and resilient water management systems and fostering awareness, engagement, demand, and applying appropriate technologies among policymakers, local authorities, community stakeholders. The chapter describes the present-day scenario of water resources in the world and Asian countries and the prevailing problems and critical issues in wastewater management. Furthermore, a comparative account of policies and initiatives by Governments of the Asian countries is detailed. Consequently, advanced techniques for wastewater treatment and prospects of reuse and recycling of wastewater adopted by industries have been addressed.

**Keywords** Pollutant discharge pattern · Policies · Sustainable water use · Industrial wastewater discharge · Circular economy

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## 17.1 Introduction

Asia ranks top in population among the global continents. Many rivers in South Asia, such as the Ganges, Brahmaputra, and Indus, have a substantial impact on economic growth, food production, ecological stability, and long-term development. Several Asian economies have shifted from relying mainly on agricultural income to relying substantially on industrial income. Mushrooming industries include food and beverages, textiles, cement, rubber products, and electrical with production increasing by 20 to 45%. Industrial activity accounts for more than 20% of total GDP of more than 30 countries in Asia (ESCAP 2005). Droughts and floods have been caused by both man-made and natural tragedies, such as poor wastewater management systems and increased pollution in water bodies (UNESCAP 2018). Domestic, industrial, and agricultural waste have contaminated the majority of water resources in Asian countries, harming human health and water quality. Most of these countries have recently experienced weed infestation and eutrophication issues, which have harmed the normal biological functioning of these freshwater bodies. The loss of aquatic biodiversity due to eutrophication is estimated to be around one-third worldwide, with the most substantial losses occurring in South Asia, Europe, China, Japan, South Asia, and Southern Africa (OECD 2012). Surface runoff and poor wastewater treatment facilities outside OECD countries pose algal blooms which are expected to rise by 20% by 2050 (OECD 2012).

Scarcity of water and pollution affect both developed and developing countries (OECD Environmental Outlook to 2050, OECD 2012). To prevent contamination in receiving water bodies, tougher measures or legislation are urgently needed. In addition, to address the current water scarcity, more advanced and effective wastewater treatment procedures are required. The current study examines the current state of wastewater treatment procedures in Asian countries as well as their future prospects. Legislative strategies in Asian countries to conserve and effectively utilise water resources must be established. The water issue in developing countries has worsened as a result of unsustainable water consumption and poor management. The water situation is becoming more complex as a result of excessive water consumption and poor management in emerging countries (Shan et al. 2020). Asian countries are initiating sustainable methods of water management with emphasis on environmental legislation (Alexandra et al. 2012).

## 17.2 Present-Day Scenario of Wastewater Management in the World and Asian Countries

Due to urbanisation, most industrial sectors have expanded their production up to 20–45%. This increase in production has led to vast volumes of wastewater discharged untreated into the water bodies.

Asian countries in the north and south such as Mongolia, Kyrgyzstan, and Azerbaijan have high BOD/GDP rates (10 kg BOD/US$1000 GDP) exhibiting the greatest levels of industrial pollution. BOD emissions per US$1000 GDP are lesser in Bangladesh and Nepal (8 kg) and Sri Lanka and Cambodia (7 kg) (5 kg). BOD/GDP rates in other Southeast Asian countries are less than 4 kg/US$1000 GDP (ESCAP 2005). Southeast Asia's water bodies are said to be the most heavily polluted with heavy metals and harmful compounds in the region (ADB 1997). Mining is a major source of anthropogenic atmospheric mercury, with Asia being the largest producer. It accounts for over half of all world emissions (Li et al. 2009). Pakistan's industrialisation is putting a strain on the country's water supplies (ADB 2008).

In India, wastewater treatment remains a major concern, particularly in rapidly growing metropolitan areas. Only 36% of total wastewater has been efficiently treated in cities of grades one and two, according to CPCB reports ( 2013, 2017) Furthermore, just 13.5% of sewage is successfully processed, compared to 18.6% of total capacity in 2017 (CPCB 2013, 2017; Schellenberg et al. 2020).

Strokal et al. 2021 investigated the effects of urbanisation on future river pollution using a multi-pollutant method for the years 2020, 2050, and 2100. They used a multi-pollutant methodology to correlate population densities, wastewater treatment levels, and a multi-pollutant methodology to assess the effects of rising urbanisation on future global river quality. Correlation between microplastics, pathogens, and point source nutrients of 10,226 rivers was studied. River pollution is at an all-time high in Europe, Southeast Asia, and North America, according to them. More than 80% of the global population is predicted to live in sub-basins with multi-pollutant problems in the future, according to high urbanisation scenarios. River pollution in Africa is anticipated to be 11–18 times worse in the future than it was in 2010, making it harder to accomplish the Sustainable Development Goals. Improved wastewater treatment makes it theoretically possible to avoid future contamination in many regions.

Heavy metal concentrations in rivers are also creating a serious hazard because they are not treated like wastewater. Asia, Africa, and South America projected high metal concentration than European and North American counterparts exhibiting different sources across all continents with Africa dominating fertiliser and pesticide use, as well as rock weathering. In Asia and Europe, manufacturing industries and mining were dominating (AWDO 2020, Environmental Water Security).

According to the 2010 UNEP/UN-HABITAT Sick Water Report, densely populated coastal areas create up to 90% of untreated wastewater flows, polluting rivers, lakes, groundwater, and coastal waterways. Water produced by agriculture and animal operations poses a significant issue for downstream consumers since it contains organic and inorganic contaminants originating from fertilisers, pesticides, human waste, livestock dung, and minerals. Similarly, heavy metal pollution, man-made organic pollutants, and micropollutants like pharmaceuticals cause problems in wastewater generated by mining and industry.

In addition to these multiple obstacles, particularly in developing nations, financing, running, and maintaining wastewater treatment infrastructure is a substantial impediment. The cost of installing centralised wastewater treatment plants is often high. Investments in modern water and sewer systems are expected to cost roughly $30 billion per year by 2025, with prices rising to $75 billion (excluding operation and maintenance costs).

In centralised systems, wastewater transport and treatment facilities must be constructed to accommodate these erratic high flows. Through 2015, it is anticipated that developing nations will require $103 billion in funding for water, sanitation, and wastewater treatment. Brazil, China, and India, for example, have already devoted enormous resources to infrastructure development (Privatization Law No. (25) of Jordan, enacted in 2000).

## 17.3 Policies and Initiatives by the Government of Asian Countries

Wastewater treatment is vital for protecting human health from viruses and dangerous contaminants. International conventions like the Basel Convention on Hazardous Waste, the Rotterdam Convention on hazardous Chemicals and Pesticides, and the Stockholm Convention on POPs (Persistent Organic Pollutants) provide governments with the legal and monitoring tools they need to regulate substances entering waterways and protect public health and the environment (UNEP 2015). Municipalities must collect wastewater and decide whether to treat it intensively (mechanically) or broadly (chemically) (using wetlands, for example). Local environmental conditions like temperature, rainfall, resources availability (human, capital, geographical extent, raw material), cultural differences must be taken into consideration while adopting centralised or decentralised wastewater management system (UNEP 2015). The rising expenses of wastewater management should be altered to offset the operating and maintenance costs. For each geographical area, appropriate criteria for applying the ‘polluter pays’ principle must be defined based on end uses and effluent quality, as well as economic and social variables. The cost of treating and selling treated wastewater to end-users must cover the cost of delivery and maintenance at the very least (UNEP 2015).

Recently treated wastewater has been used for agriculture purpose. According to estimates of Sato et al. (2013), lower-middle-income countries (LMIC) and least developed countries (LDC) treat 28 and 8% of their generated wastewater, respectively. Some wealthy countries, on the other hand, have made headway toward treating all water. The limited treatment capacity of countries is due to two key factors. To begin with, the costs of treating wastewater are extremely expensive. For example, the total expenditure planned for tertiary and secondary treatment plants is EUR 14,800 million and EUR 2091 million, respectively (Kumar and Tortajada 2020). Second, in these countries, solid waste management takes precedence over wastewater treatment, with different degrees of treatment. Recycled water as an alternative source can help close the gap between supply and demand for water. Previously, wastewater was primarily used for irrigation and other agricultural reasons, with narrow attention on recycled water for various purposes within cities. Despite advancements in technology and legal frameworks, little progress has been accomplished in these economically backward nations. Below is a discussion of several Asian countries wastewater regulations and initiatives summarised in Table 17.1.

**Table 17.1** Policies of Asian countries for wastewater management

| Sr no | Country | Policies/initiatives | References |
|---|---|---|---|
| 1 | Russia | (a) Water technology transfer from developed countries<br>(b) Use of non-conventional resources—desalination<br>(c) The federal government motivated large business owners to establish PPPs (public–private partnerships) | Wei (2015) |
| 2 | China | (a) Comprehensive reform to convert resource fees to resource taxes | Guo et al. (2018a) |
| 3 | India | (a) National Water Policy (NWP) 2012<br>(b) Recycling of treated wastewater (2018) | Vij et al. (2021) |
| 4 | Saudi Arabia | (a) Inadequate infrastructure limits the recycling of partially treated wastewater<br>(b) Use of non-conventional resources—desalination | Alkhudhiri et al. (2019) |
| 5 | Turkey | (a) Ministry of Environment and Urban development, Turkey has prepared an action plan for wastewater treatment for the years 2015–2023<br>(b) MoEU initiated the project, 'Reuse of Treated Wastewater in Turkey' | Maryam (2017) and Nas et al. (2020) |
| 6 | Indonesia | (a) National Policy of Wastewater Management in Indonesia encourages efforts to reuse/recycle domestic wastewater treatment products<br>(b) Wastewater resource recovery (WRR) | Yudo and Said (2017)<br>Marleni and Raspati (2020) |
| 7 | Korea | (a) Any building with more than 60,000 m2 of total floor space is required to install a water reuse system by law. However, only less than 0.5% of the total buildings have more than 10,000 m2. Therefore, the regulation is ineffective and merely nominal.<br>(b) Inexpensive service water discourages the use of recycled water | Noh et al. (2004) |
| 8 | Japan | (a) Direct penalty system<br>(b) Low carbon footprint | Hosomi (2016) |
| 9 | Pakistan | Lack of national policy and economic incentives | Batool and Shahzad (2021) |
| 10 | Thailand | Enhancement and Conservation of National Environmental Quality Act, (1992)—service fees shall be used as expenditures for operation and maintenance of the central wastewater treatment plan | Chevakidagarn (2006) |

### *17.3.1 India*

Over the years India has realised the potential of water as a necessary resource for economic development and basic human need. According to the Ministry of Environment, Forestry, and Climate Change only 37% of wastewater is treated out of 62 MLD generated from towns and cities (Vij et al. 2021).

India's first National Water Policy adopted in 1987 merely established the pollution control boards at central and state level. Later in 1974 and 1977 the Water pollution act and Water Cess act helped in preventing water pollution and maintaining the water quality. Later in 2002 the policy was revised with discharge limits defined in line with the principle of polluter pays.

Later in 2008 the focus shifted to sanitation and potable drinking water for all which led to adopting the National Urban Sanitation Policy (NUSP). Insufficient funds hindered the goals of the policy. This led to introduction of various finance schemes by government in later years. The Urban Infrastructure Development Scheme for Small and Medium Towns (UIDSSMT), Jawaharlal Nehru National Urban Renewal Mission (JNNURM) were some of the notable attempts. Although the lack of participation methods utilised in the construction of projects under these schemes has been criticised, these programs boosted the participatory and democratic government concepts (Kundu 2014).

Later in 2011 the Clean Ganga mission was established to treat sewage across the Ganga basin. Furthermore, the new policy of 2012 addressed climate change issues, water scarcity, and the economic value of water. Reuse and recycle of treated water being the primary goals of the policy. In 2016 bilateral Collaborations of Central Public Health and Environmental Engineering Organisation (CPHEEO) and Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) resulted in awareness of cities towards sustainable water management (3R, 2016 CPHEEO).

Despite the fact that the Central/State Pollution control board (CPCB/SPCB) develops wastewater guidelines and manuals to ensure that water quality standards are met in India, policy implementation has been weak. According to one respondent, this is mostly due to a lack of human resources, inadequate state laboratories for evaluating pollutants and weak legislations (Starkl et al. 2013). The Gujarat state government stated in May 2018 that it has adopted the Reuse of Treated Waste Water Policy, which requires all power plants and significant enterprises within 50 kilometres of a sewage treatment plant to use recycled wastewater to reduce the pressure on groundwater and surface water. In Gujarat, industrial associations have successfully implemented PPP models using treated recycled wastewater. In this context, other states such as Punjab, Jharkhand, and Karnataka have altered their state water policy.

Currently Ministry of Environment, Forest and Climate change (MoEFCC) and CPCB are the nodal agencies for developing policies and regulating standards along with the newly formed Ministry of Jal Shakti (Schellenberg et al. 2020).

### 17.3.2 Russia

Russia's total freshwater consumption from water bodies is substantial, at around 70 billion $m^3$ per year. Southern Russia is major consumer of water for nuclear power plants, various heat supply and manufacturing industries along with agriculture. Following the 1998 economic crisis, the Russian government 'froze' utility service pricing for 1999–2000. After 2003, however, the federal government urged significant business owners to create public–private partnerships by sharing risks of disasters and ultimately reviving the treatment scenario in their municipality. The discharged water contained nitrates, phenols, mercury, and some untreated wastewater. Only 61% of the entire volume was remediated that met the guidelines (Russian Federal State Statistics Service 2017). On an average the utility and agricultural sector discharged over 90% of hazardous compounds due to inefficient treatment facilities (Gazeta 2010).

Water technology transfer (WTT) from developed nations may be expedited as a result of green economy aims, while WTT from underdeveloped countries may be accelerated as a result of increased foreign investor like China (Wei 2015). The conversion from chlorine-based treatment to UV and membrane treatment spread across entire Russia, as it has been in several other nations (for example, Saudi Arabia). About 30% seaports utilised treated sewage for domestic purpose.

### 17.3.3 China

Prior to 2015, China's Wastewater Discharge Fees were based on treatment costs. Low discharge costs resulted in excessive wastewater contamination and minimal water prices did not encourage businesses to recycle water, alleviate consumption, and reduce wastewater outflow. From 41.5 billion tonnes in 2000 to 73.5 billion tonnes in 2015, China's total wastewater output has gradually increased (Ao et al. 2020). With the prevailing issues China reconsidered its environmental laws pertaining to wastewater discharge.

The Chinese government has recently emphasised the role of markets in resource allocation and reformed the tax system by launching a comprehensive scheme, with Hebei serving as the pilot province (Cao et al. 2016). The Water Resource Taxes were reformed by concerned ministries. Later in 2018, the water tax (Environmental Protection Tax Law) came into effect. The state administration distinguished taxes and fees on three contexts. First, the tax authorities, customs, and fiscal authorities are the main tax-collection bodies representing the state, while fees are collected by sector administrations. Second, tax rates are fixed, whereas fee payments are determined by treatment costs. Lastly, fee earnings are used to conserve water, whereas tax revenue can be used for any purpose by the state. China used to regulate water resource levies that were expressly utilised for water conservation prior to the transition. However, there are certain issues with payment, such as a lack of understanding of the need to pay fees and the lack of necessary collection mechanisms, to name a few (Guo et al. 2018b).

China had issued over 60 sound and enhanced pollutant discharge guidelines for industrial wastewater by 2018. Based on previous achievements and foundations, China is entering a new era of wastewater treatment, with water recycling and resource recovery options from sludge becoming the primary objectives.

### *17.3.4 Pakistan*

Pakistan's challenges include a lack of policies and adequate economic incentives from the government responsible for infrastructure and institutional failures, fixed water prices, and a scarcity of resources. In Pakistan, water is plentiful, and there appears to be no effluent discharge policy or industrial treatment incentives (Batool and Shahzad 2021).

### *17.3.5 Japan*

The Water Pollution Control Law in Japan establishes effluent standards (Uniform National Effluent Standards) for defined enterprises across the country that are uniform across all industries. The control is done through a method known as the 'direct penalty system', which allows for penalties to be imposed solely because of excessive concentrations.

Almost three quarters of domestic sewage in urban areas of Japan is being treated in centralised STPs. It is estimated in one of the Central government report that the annual power requirement for operating the treatment plants requires seven billion kWh which is approximately equivalent to the output of nuclear power plant of capacity of one million kWh. This quantity of electricity usage accounts for 0.7% of Japan's total electric power consumption.

In addition to energy savings, greenhouse gas (GHG) emission reduction is critical in a wastewater treatment facility. In Japan, sewerage utilities release seven million tonnes of $CO_2$ per year, accounting for 0.5% of total $CO_2$ emissions. Regulatory controls on GHG emissions and nitrous oxide should be considered as potential targets in coming future. Paradigm shifts towards low ecological footprints with cost-effectiveness and better operating performance shall be included in the present strategy for wastewater management (Hosomi 2016).

### 17.3.6 Korea

It is predicted that with high water resources demand of 38 billion tonnes by 2020 shall be impossible to be met by Korea's present resource capacity. The obvious solutions to cope with the present scenario are reduced water consumption and optimum recycling of wastewater. In total, the country has 99 on-site water-recycling systems. The 99 systems have a total capacity of 429 thousand tonnes per day. In comparison to the remaining industrialised countries, Korea has a small number of water-recycling systems. The following are the key causes for this. To begin, every building in Korea that has a total floor area of more than 60,000 $m^2$ is obliged by law to incorporate a water recycle system. However, only about 0.5% of all structures are larger than 10,000 $m^2$. As a result, the regulation does not serve any purpose. Next, water is provided at a nominal cost (0.20 US dollars per cubic metre of water). People are typically discouraged from recycling treated wastewater because of the low cost of service water. Third, some individuals believe that recycled water is not clean enough and can lead to disease. As a result, people should be convinced of use of reusable grade of treated water that is generated by a properly managed recycling system (Noh et al. 2004).

### 17.3.7 Indonesia

Indonesia confronts issues as a result of its population expansion, which reached 280 million in 2017 and is growing at a rate of 2% per year. Two-thirds of Indonesia's population will reside in cities, according to estimates (Indonesia and Statistik 2012–2013). The alarming population growth and congested locations threaten the availability of sufficient food resources and water resources that sustain life. Furthermore, a dense population has an adverse effect on the environment due to the excessive outflow of both treated and untreated effluent (Cordell et al. 2011; Gerbens-Leenes et al. 2010; Thornton 2010).

Untreated sewage has accelerated environmental degradation; however, some reports indicate stabilisation or even slight gains in only a few sites. Yudo and Said (2017) quoted a report submitted by the Ministry of Environment and Forestry that almost 75.2% of rivers are extremely contaminated. However, the government is still banking on the valuable resources in form of precious elements, electricity, nutrients, recycled water that can be recovered for the benefit of the society. The government policies in Indonesia support efforts to reuse/recycle residential wastewater treatment products along with regulatory disposals of the same (Yudo and Said 2017). The Wastewater Recovery (WWR) technique is being promoted by the government. The wastewater treatment fee is modest, which may encourage people to discharge rather than collect their effluent (Marleni and Raspati 2020).

### *17.3.8 Saudi Arabia*

Saudi Arabia relies solely on desalinated water, surface water, and groundwater as there are no permanent water resources such as rivers or water bodies. Water scarcity is a serious issue in an arid region with limited water resources. The population rose by 3% in 11 years from 25 million to almost 33 million by 2018. In addition, freshwater consumption has risen considerably in the last 20 years. As a result, recovered wastewater and water conservation are viewed as strategic alternatives. The total sewage output is expected to reach 830 million $m^3$ per day by the end of 2019. Several more wastewater treatment plants will be built by 2019, bringing the overall number to around 95. These treatment plants will be capable of treating 2.8 billion $m^3$ of sewage per year. Because of a lack of incentives and inadequate treatment, wastewater could not be used as a substitute for natural water in the 1990s. In addition, the wastewater treatment infrastructure was insufficient to meet all demands. As a result, in Saudi Arabia, the reuse of cleaned wastewater was a controversial topic. According to Chowdhury and Al-Zahrani (2015), around 40% of wastewater is discharged untreated. Furthermore, in Saudi Arabia at the time, secondary treatment technique was the most often employed (Ouda 2015). With government approval, tertiary treatment is now used for all forms of wastewater, including domestic, industrial, and agricultural.

Desalination is viewed as a strategic solution to Saudi Arabia's water problem. Although the Saline Water Conversion Corporation (SWCC) ranks first in the production of desalinated water, the desalination industry confronts challenges such as crude oil dependence and brine management (Alkhudhiri et al. 2019).

### *17.3.9 Turkey*

In terms of present water potential, Turkey is not a water-rich country. Its major water resource comes from rivers (86% of 112 billion $m^3$) and remaining 14% comes from groundwater resources.

The government has set up limited discharge criteria and levied taxes and fines for managing the wastewater. The Turkish Ministry of Environment and Urbanisation (MoEU) created a Strategy for Wastewater management for the years 2015–2023, which included monitoring of water quality and estimating quantity in Turkey's river basins, modelling approaches, and certain critical physicochemical characteristics. In 2016, the Ministry of the Environment undertook a survey to assess the state of wastewater treatment in Turkey across households of the country. According to the initiative, municipalities create 82.9% of treated wastewater, which grew to 85% in 2018. In the year 2023, Turkey's optimum rate for municipal wastewater treatment will be 100%. The second major initiative, 'Reuse of Treated Wastewater in Turkey,' was launched by the MoEU in 2017. The goal of this project is to evaluate the present standards and practices of the wastewater treatment as compared to global methods as well as formulate legislative policies for the reuse of treated wastewater in Turkey. As part of this research, all WWTPs were examined for the first time for wastewater reclamation and reuse reasons (MoEU and SU 2016; Nas et al. 2020).

### *17.3.10 Thailand*

Thailand follows the Enhancement and Conservation of National Environmental Quality Act of 1992, which states that the Pollution Control Department (PCD) of the Ministry of Natural Resources and Environment (MONRE), which looks after the functioning of public wastewater treatment plant, has the authority and responsibility to collect penalties and fines. The service fees will be utilised to pay for the central wastewater treatment plant's operation and upkeep (Chevakidagarn 2006). Currently, wastewater from 66 million people pollutes 9.9 million $m^3$ of water per day, of which only 33% is being treated by about 100 WWTPs. According to inspection and law enforcement with pollution sources merely 48% comply to the standards.

## 17.4 Prevailing Problems and Critical Issues in the Wastewater Management

Inadequate institutional capacity to keep pace with industrial revolution has resulted in stringent water quality regulations in emerging economies. (Kathuria and Sterner 2006) and economic measures like taxes and the removal of fertiliser grants conflict with other development aims. Voluntary compliance is seldom achieved when monitoring is an expensive affair (Evans et al. 2012). The significant issues in wastewater treatment are divided into three broad categories: Inefficient treatment technologies, chemicals that escape treatment, and management flaws. A summary of the above issues is given in Table 17.2.

### *17.4.1 Inefficient Treatment Technologies*

Operational efficiency is becoming increasingly important in many industries, but particularly in water treatment operations. There are numerous advantages to improving efficiencies within wastewater treatment plants in order to control costs and comply with increasingly stringent regulations (Brentagg websource).

Current wastewater treatment procedures are inefficient due to a heavy reliance on biological treatment systems that cannot withstand shock loads (Brentagg

**Table 17.2** Common problems of inefficient wastewater treatment

| Sr no | Categories | Problems |
|---|---|---|
| 1 | Inefficient treatment technologies | (a) Wear and tear of plant structures<br>(b) Variable flow<br>(c) Variable turbidity<br>(d) Scale build-up<br>(e) High BOD<br>(f) Pin floc<br>(g) Sludge management |
| 2 | Chemicals that escape | (a) High nutrients<br>(b) Excessive FOG (fats, oil, and grease)<br>(c) Microplastics<br>(d) Xenobiotics/recalcitrants (broad-spectrum antibiotics and PPCPs)<br>(e) Heavy metals<br>(f) PFAS (per/poly-flouroalkyl substances) |
| 3 | Management flaws | (a) Lack of advanced technologies in developing countries due to high capital investment<br>(b) Centralised/decentralised systems<br>(c) Lack of skilled supervisor/operators<br>(d) Lack of maintenance<br>(e) Inadequate monitoring system |

websource). Energy consumption is one of the most pressing issues confronting wastewater treatment plants. The massive carbon footprint and maintenance costs of these systems render wastewater treatment unsustainable and expensive (Brentagg websource). Some of the major issues that contribute to treatment inefficiency are as follows:

#### 17.4.1.1 Wear and Tear of Plant Structures

Higher turbidity and hardness of the water cause erosion of concrete surfaces which add to the maintenance cost, reduce operational efficiency and life of equipment. The use of more resistant to erosion materials and designs in plants has become unavoidable.

#### 17.4.1.2 Variable Flow

Inefficient solids removal is caused by hydraulic overloading. Wastewater treatment plants must deal with a constantly changing flow rate. Peak demands can be met with automated chemical feed systems and the installation of holding tanks, which would require additional capital investment.

#### 17.4.1.3 Variable Turbidity

Another issue is turbidity, which refers to the cloudiness of water caused by the presence of particles. If not handled properly, turbidity variation can have a severe impact on process result in failure of meeting quality standards. It might also result in more sludge being created. Turbidity fluctuation can be accommodated by designing a treatment system that is slightly larger. Automated chemical feed systems and sludge handling system oversizing can also help accommodate turbidity changes.

#### 17.4.1.4 Scale Builds Up

Scaling caused by impurities such as silica, magnesium, calcium, iron, aluminium, and others can hinder treatment operations (Brentagg websource). Scaling hinders flow of water through the system, thereby increasing power consumption and alleviating overall efficiency. Speciality chemicals such as scale inhibitors can efficiently prevent scale build-up, which saves time and money.

#### 17.4.1.5 High BOD

To prevent oxygen depletion in waterways, regulations ensure that biochemical oxygen demand (BOD), a measure of the number of organics in water, remains at particular levels (Brentagg websource). Keeping up to the oxygen demands encountered during high BOD is a difficult task. Advances in diffuser installation to meet such demands require attention. Aeration of the waste stream, which increases biological oxidation, can help wastewater plants regulate BOD (Brentagg websource). Solids would be produced by this process, which might be removed by filtration or clarifying.

#### 17.4.1.6 Pin Floc

Wastewater treatment plants employ flocculants to collect particle suspended materials into floc clusters, which can then be removed from the water (brentagg websource). The flocculation process is an important aspect of the wastewater treatment process. Poor settleable pin floc particles alleviate the sedimentation of the solids making it difficult to remove them (Brentagg websource). In cases of excessive underloading or the presence of poisonous compounds that could generate pin-flocs and lead to unsatisfactory treatment, settling aids will be required.

#### 17.4.1.7 Sludge Management

A byproduct of the sedimentation process at the primary and secondary treatment stage contains nutrients and organic matter, making it sound like a fertiliser in the agriculture industry. Sludge often poses a disposal issue because of large quantities in generation and hazardous nature. Hence plants must discover long-term, safe, and sustainable sludge management solutions.

### *17.4.2 Chemicals That Escape Treatment*

Many of the chemicals in wastewaters now originate in our houses and are leached from products or are directly added in the case of cleaning products and excreted drugs, according to research (UKWIR 2018). Concerns are developing about the existence of chemical mixes in the environment, dubbed the ‘cocktail effect’, which may be affecting aquatic life (EEA 2019). Antimicrobial resistance (AMR), which results from the use of antimicrobials such as antibiotics in human and veterinary treatment, is one example of potential new risk. Antimicrobial usage and excretion have resulted in the emergence of resistant bacteria, viruses, and microorganisms that can cause disease and are now resistant to therapy. During tertiary treatment, physical separation and membrane-based techniques are used to remove the remaining inorganic compounds (ammonium, sulphate, and phosphate) and other xenobiotics (Liu 2017).

#### 17.4.2.1 High Nutrient Levels

The presence of nutrients in partially treated waters being discharged into rivers causes eutrophication. The water treatment systems need to implement nutrient reduction processes to safe levels in order to overcome this issue. This necessitates considerable process adjustments, such as anaerobic and/or anoxic treatment of a section of the aeration basin, which reduces aerobic volume and limits nitrification capabilities.

#### 17.4.2.2 Excessive FOG

Water does not mix well with fats, oils, and grease (FOG). FOG levels in wastewater that are unusually high can cause serious complications. If discharged inappropriately it has the potential to choke pipelines and infrastructure, increase BOD, float to the top, etc. (brentagg websource). FOG levels that are unusually high may limit oxygen from reaching the water, resulting in septic conditions (brentagg websource). Excess FOG must be removed by chemical or mechanical means, which is both inconvenient and expensive.

#### 17.4.2.3 Microplastics

Plastics end up in the environment as a result of either a single source of contamination or a widespread contamination. Vermeiren et al. (2016) reported various non-point sources of microplastics including agricultural runoff, industrial spills, and air depositions. Each year, oceans receive up to 2.41 million tonnes of microplastics from rivers (Lebreton et al. 2017). Microplastics, particularly fibres, have been recognised as a key source of microplastics at wastewater treatment plants (WWTP) (Browne et al. 2011). Cosmetics and personal care goods, plastic products such as textiles, and automobile tyres or road paints are among the sources of plastic debris that reach WWTP. Microplastics reach WWTPs via home wastewater or drainage systems, where they may be released into bodies of water or scattered with sludge (Ngo et al. 2019). According to several research, WWTPs have high rates of microplastic removal, frequently exceeding 95%. Despite the fact that sludge has absorbed the majority of the microplastics, the remaining fraction is still significant (Sun et al. 2019; Lv et al. 2019).

Furthermore, WWTP sludge is commonly used as a soil amendment in agriculture due to its high nutritional value (Gherghel et al. 2019). Recycling wastewater and sludge supports the circular economy concept; however, they reintroduce microplastics into the ecosystem, posing a significant environmental risk (Gatidou et al. 2019). Inadequate understanding of lifecycle of tiny plastic particles and fibres in the WWTPs warrants a debate about how much water discharges and sludge management contribute to microplastic buildup in environmental compartments (Carr et al. 2016).

#### 17.4.2.4 Xenobiotics/Recalcitrants

Spongberg and Witter (2008), Palmer et al. (2008), Vieno et al. (2006), and Bendz et al. (2005) reported that majority of xenobiotics enter the aquatic environment via domestic sewage treated in conventional treatment plants. The inefficient traditional WWTPs discharge considerable quantities of many xenobiotics due to inadequate biological degradation and high levels of raw influences in secondary treatments. An important source of recalcitrant xenobiotics contains broad-spectrum antibiotics. Because many pesticides are poorly biodegradable and very hydrophilic, they are of special concern. The ability of convectional wastewater technology to process these impurities may be limited (Armah et al. 2020).

Verlicchi et al. (2010) and Martin Ruel et al. (2010) reported the effectiveness of advanced techniques of nanofiltration (NF), ultraviolet (UV) or ozone and reverse osmosis (RO) in removal of more than 90% of xenobiotics that were previously poorly removed in WWTPs. However, these procedures are not ‘environmentally friendly’ (Wenzel et al. 2008; Høibye et al. 2008) and lack sustainability. Overcoming difficulties such as the treatment of RO concentrates and of hazardous metabolites during ozone oxidation need adequate research (Verlicchi et al. 2010).

Broad-spectrum antibiotics, pharmaceuticals, and personal care products (PPCPs) have inherent ability to cause physiological effects in low doses (Ebele et al. 2017). A growing number of studies have established the presence of numerous PPCPs in diverse environmental compartments, raising worries about possible negative consequences for humans and wildlife.

#### 17.4.2.5 Heavy Metals

Heavy metals, usually referred to as trace metals, are among the most persistent contaminants found in wastewater (Akpor et al. 2014). Metals, primarily from the textile, mining, and manufacturing units are commonly found in wastewater. Baysal et al. (2013) reported the most common metals found in industrial wastewaters, namely arsenic, lead, sodium, aluminium, mercury, iron, chromium, nickel, copper, tin, potassium. Heavy metals are commonly found in wastewater from mining and foundries followed by microelectronics and textiles. High remediation costs pose a variety of environmental issues such as plant growth distortion, algal bloom, aquatic biota death, debris development, and sedimentation (Akpor et al. 2014). Burakov et al. (2018) reported cancer, skin disorders, multiple organ failures, respiratory illness, and nervous disorders as human health impact. Bioaccumulation of metals in wastewater even at trace concentrations (1–3 mg/L) is hazardous (Baysal et al. 2013; Al-Saydeh et al. 2017).

#### 17.4.2.6 Per-/Poly-Fluoroalkyl Substances (PFAS)

These are a new class of environmental pollutants that are employed as additives to improve product thermo-chemical stability or alter surface qualities. PFAS are amphiphilic compounds made up of fluoroalkyl chains terminated by carboxylic, sulphonic, phosphate, sulphonamide, and betaine functional groups. It has surfactant-like properties, making it highly persistent and mobile in various types of environments. The complexity of the wastewater matrix coupled with low quantities renders inefficient removal of the PFAS. Trace exposure of PFAS can have serious impacts on the health of all living beings (Garg et al. 2021).

PFAS (perfluoroalkyl sulfonates) values of 124.95 g/day (PFAS: 49.81 g/day; PFCAs (perfluoroalkyl carboxylates): 75.14 g/day) have been observed from eight WWTPs in Japan and 55.04 g/day (PFASs: 12 g/day; PFCAs: 43.04 g/day) from five (Shivakoti et al. 2010). The Han and Nakdong Rivers received 89% of the total PFAS discharge from WWTPs in Korea, according to the projected total daily mass of emitted PFCs (Kwon et al. 2017).

## 17.5 Advanced Techniques for the Treatment of Wastewaters Adopted by Industries

Toxins, phosphorus, nitrogen, and heavy metals are not entirely removed from contaminated wastewater using conventional treatment processes. Despite the fact that all of these elements make them expensive and time-consuming, these processes help to reduce the levels of myriad pollutants to some extent and each has its own set of benefits and drawbacks (Jain et al. 2021). The next sections detail some of the advanced strategies used by industry to overcome the difficulties stated at the beginning of the chapter.

### *17.5.1 Techniques to Overcome Operational Difficulties*

Installation of holding tanks and automated chemical feed systems can be used to manage peak demands which would prevent short-circuiting issues. Designing an oversized treatment system shall help accommodate turbidity variation. The use of scale inhibitors can save energy and maintenance costs by preventing build up in equipment. Overcome pin-flocs by use of appropriate coagulants and polyelectrocytes shall enhance the solid removal.

### *17.5.2 Techniques to Treat Persistent Chemicals and Microplastics*

#### 17.5.2.1 Advanced Oxidation Technologies

Some pollutants contained in wastewater are resistant to treatment using physical and chemical methods. Chemical oxidation techniques can supplement conventional treatment methods by introducing transformations that use oxidation and reduction reactions to eliminate stubborn substances.

In the wastewater treatment sector, the advanced oxidation method is gaining favour. The hydroxyl radical is the major focus of this mechanism, which, once created, destroys practically all organic molecules vigorously. To remove recalcitrant organic molecules, photocatalytic ($TiO_2$/UV) processes, ozonation, $H_2O_2$/UV processes, and Fenton's reactions have all been employed extensively (COD, TOC, dyes, and phenolic compounds). These processes are influenced by primary pollutant concentrations, oxidants, catalyst quantity, light intensity, irradiation period, and the makeup of the wastewater solution (pH, TDS, and other ions). It has been determined that doing pilot plant studies is required for estimating capital costs, overhead, and management prices since pilot plant studies are better equipped to provide closer circumstances for estimating correct costs. $H_2O_2$/$O_3$ and $H_2O_2$/UV appear to be the two most promising AOP systems based on the limited reviews and they are both economically viable (Krishnan et al. 2017).

#### 17.5.2.2 Advance Anaerobic Sludge Digestion Processes

Because it takes up less space, produces less sludge, and produces renewable energy in the form of methane, anaerobic digestion has been lauded as the most environmentally friendly wastewater treatment technology. Anaerobic baffled reactors (ABR), sequencing batch reactors, and up-flow anaerobic sludge blanket (UASB) reactors are now used to treat oily wastewater (Kuyukina et al. 2020). However, anaerobic treatment is insufficient to meet water discharge criteria, necessitating further treatment, such as aerobic treatment (Wang et al. 2017). PAHs were removed from refinery wastewater using a laboratory treatment system that included UASB and aerobic packed-bed biofilm (PBB) reactors (COD of 435 mg/L; TPH of 1520 mg/L; PAH of 10.33 mg/L), yielding an overall COD removal efficiency of 81.07% and complete removal of three PAHs (naphthalene, phenanthrene, and pyrene) after 118 days (COD of 435 mg) (Nasirpour et al. 2015).

#### 17.5.2.3 Membrane Bioreactors

Over the last century, membrane bioreactor (MBR) technology has surpassed the traditional activated sludge process (ASP) as the preferred wastewater treatment technology (Ramachandra et al. 2006).

Over the last century, membrane bioreactor (MBR) technology has been a growing wastewater treatment method (Ramachandra et al. 2006). Ultrafiltration, reverse osmosis, and nanofiltration are examples of membrane filtration processes that have been widely used. Nanofiltration, photocatalysis, adsorption and biosorption, disinfection treatment and pathogenic control, sensing, and monitoring are all nanotechnology-based wastewater cleanup approaches. Membrane bioreactor (MBR) technology has lately gained popularity as a treatment method in wastewater treatment plants. It performs exceptionally well in the removal of microplastics (removal effectiveness of 99.9%) (Talvitie et al. 2017).

However, the use of nanotechnology in wastewater treatment is subjected to the systematic investigation of possible biological and ecotoxicity associated with their use. Membrane fouling is most common drawback of the membrane filtration which can be overcome by physical cleaning, using biocides, acid, and bases.

Advanced treatment technologies including as UV or ozone oxidation, nanofiltration (NF), and reverse osmosis (RO) have been shown to improve treatment for the majority of xenobiotics that are difficult to remove in typical WWTPs, with removal efficiencies of over 90% (Verlicchi et al. 2010; Martin Ruel et al. 2010). These procedures, however, are not ‘environmentally friendly’ (Wenzel et al. 2008; Høibye et al. 2008) and cannot be made sustainable unless a number of concerns, such as the treatment of concentrate by RO/NF processes or the generation of hazardous metabolites during ozone oxidation, are handled (Verlicchi et al. 2010).

Chemical precipitation, lime coagulation, ion exchange, reverse osmosis, and solvent extraction are all typical methods for extracting metal ions from aqueous streams (Rich and Cherry 1987). Biosorption is the process of removing chemical species from biological or natural materials as sorbents through extracellular and intracellular bonding, which is influenced by the nature of the organic compound, the structure of adsorptive materials, the microbial metabolism, and the transport process. Adsorption, absorption, ion exchange, precipitation, and surface complexation are some of the mechanisms involved in the biosorption process (Gorduza et al. 2002; Gadd 2009).

Biosorption is an economical and efficient alternative to traditional wastewater treatment plants, using living or dead biomass in static or dynamic conditions. Process efficiency has been shown to be effective in retaining both inorganic and organic compounds found at low quantities in various industrial wastewaters (Suteu et al. 2012). Microalgal biosorbents, Biochar, microbial biosorbents, etc. are being researched upon in recent times.

#### 17.5.2.4 Phytoremediation

For the cleanup of diverse industrial effluents, phytoremediation is a potential green method. In their investigation on textile effluent from Surat CETP, Sidi and Mesania (2015) found that *Eichhornia crassipes* was the best probable bioremediator. Their investigations revealed that the plants might be utilised in the CETPs preliminary effluent treatment stage, reducing effluent treatment costs and increasing cleanup efficiency while using less dosing chemicals and generating less sludge.

A recent study looked at the phytoextraction potential of aquatic plants including *Pistia stratiotes L, Salvinia adnata Desv, and Hydrilla verticillata (L.f) Royle* for cotton textile dying unit in Tamil Nadu, India. The phytoremediation capacity of P. stratiotes L efficiently decreased pollutants from the dyeing effluent without changing the pH, according to the study. The changes in phytochemical content in aquatic plants before and after the phytoremediation procedure were validated by GC–MS analysis, particularly for ascorbic acid. The plant biomass and liquid generated during the treatment process were recovered and used for composting and watering of decorative plants, indicating that the dyeing business has a great zero-waste option (Ahila et al. 2021). These discoveries pave the path for an environmentally friendly and long-term wastewater treatment technology.

#### 17.5.2.5 Heavy Metal Removal and Reuse Techniques

Technology has advanced to the point that metal ions can now be extracted and reused from metal-contaminated wastewater. For example, in the Community Bureau of Reference (BCR) sequential extraction system, diethylenetriaminepentaacetic acid (DTPA) can remove 99.6% of $Cd^{2+}$ from wastewater (Fuentes et al. 2004). $Cu^{2+}$ can be extracted from wastewater with 99% efficiency using silica-polyamine composite materials (Fischer et al. 1999). Electrospun titania nanofibers with surface-functionalised surfaces reduce Pd2+ levels in wastewater by up to 99.9%. (Dai et al. 2016).

## *17.5.3 Tecniques to Cope with Management Flaws*

The lack of advanced technologies in developing countries is due to high capital investment. The differential investment requirements for centralised/decentralised systems pose a challenge for the countries to adopt. Lack of skilled supervisors/operators with very few local technicians skilled in operating the plants cannot cope well with the engineering and scientific problems. Additionally, a lack of maintenance and an inadequate monitoring system lead to inefficiency.

Unskilled operators coupled with complex treatment requirements warrant real-time monitoring systems that would ensure wastewater discharge standards. Most Asian countries have adopted SCADA-based water quality monitoring. A case from India has been elaborated below.

### 17.5.3.1 Online SCADA-Based Monitoring with IoT

For real-time water quality monitoring, a supervisory control and data acquisition (SCADA) system that connects with Internet of Things (IoT) technology is used. Using the Global System for Mobile Communication (GSM) module, it intends to assess water contamination, pipeline leakage, and an automatic measurement of parameters (such as temperature sensor, flow sensor, and colour sensor) in real-time. The system was used in the Tirunelveli Corporation (a metropolis in Tamil Nadu, India) to capture sensor data automatically (pressure, pH, level, and energy sensors). With the addition of additional sensors and a lower cost, the SCADA system has been fine-tuned.

The results reveal that the suggested system outperforms and generates better results than existing systems. Through GSM connectivity, SCADA obtains the real-time accurate sensor values of flow, temperature, colour, and turbidity (Saravanan et al. 2018).

The Jal Jeevan Mission is an Indian government flagship programme aimed at promoting holistic management of local water resources through the use of IoT-based sensors, flow metres, water-quality detection kits, and innovative mobile applications. It has been using innovative technology to find cost-effective ways to provide safe drinking water to every rural home in the country by 2024.

## 17.6 Future Prospects of Reuse and Recycle of Wastewater

Recent advances in wastewater management, fortunately, offer enormous promise to assist alleviate some of the challenges of water supply, pollution control, waste recycling, water-borne disease health difficulties, and environmental protection. There are several contemporary developments in wastewater management that vary depending on climatic variables, development levels, and financial resources available for investment. These findings show that, far from being a nuisance, wastewater is increasingly being viewed as a resource, thanks to advances in technology that allow treated wastewater to be used in industrial operations, irrigation, and as drinkable water.

Decentralisation is an alternative to the traditional strategy of conveying reclaimed water from a central WWTP. Zero liquid discharge (ZLD) and wastewater resource recovery (WRR) are two developing solutions that must be researched and implemented in the circular economy. This emerging approach is illustrated in Fig. 17.1.

A circular economy aims to keep material value as long as possible inside the economic system (European Commission 2021). The term ‘zero liquid discharge’ (ZLD) refers to a treatment procedure in which the plant does not discharge any effluent, thereby preventing treatment-related contamination. Other profit is that a ZLD process makes efficient use of wastewater treatment, recycling, and reuse, helping to water savings by reducing the amount of freshwater used (Ahirrao 2014).

The zero liquid discharge concept was first successfully implemented in Gujarat, India, after which it declared a policy for the reuse of recycled. The cluster of textile

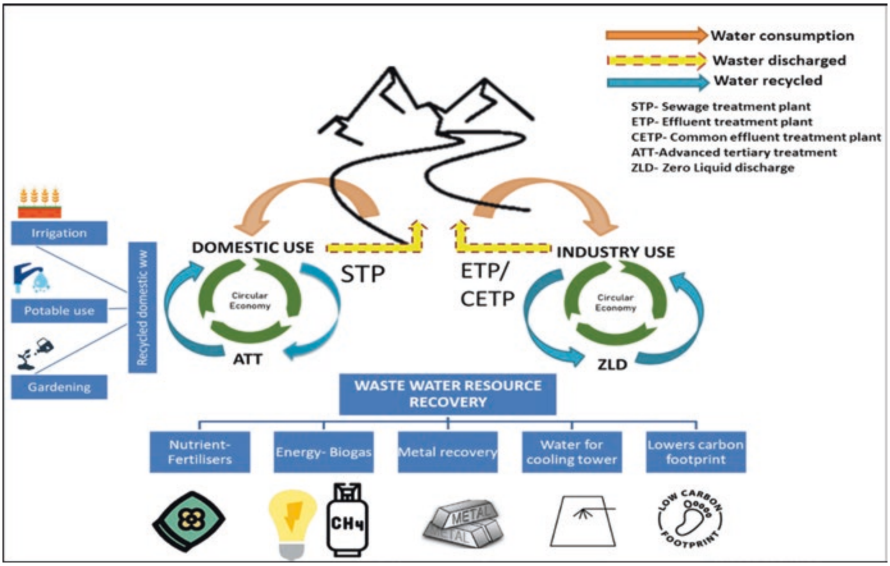

Fig. 17.1 Emerging sustainable approach of Circular economy and Wastewater resource recovery

and dyeing units in Pandesara and Bamroli came together to form an association (centralised system) to treat sewage water from the nearby areas and cater to the needs of the industries in the neighbouring GIDC. The revenue earned by member industries was utilised to maintain and operate the ETPs. CETPs later began advanced tertiary water treatment (using advanced filtration techniques) in order to recycle the water for reuse within the same industry (decentralised system). This ensures a long-term strategy for water resource management. This was a public–private cooperation (public–private partnerships). Community contractors, service contracts, management contracts, leases, concessions (build-operate-transfer), divestures, and public–private partnerships are all examples of public–private partnerships (Hutton and Wood 2013).

Due to its huge amounts, wastewater has been recognised as a resource, as it contains many valuable resources that may be transformed into valuable material. Recycling of wastewater and deriving benefits from its byproducts can reduce the impact on environment (Marleni and Raspati 2020).

Wastewater treatment plants (WWTPs) play an instrumental role within the water-energy nexus as they remove pollutants with large energy consumptions and overall reduced environmental impacts (Gu et al. 2016; Xu et al. 2017). Over the last few decades, wastewater treatment has aimed to improve sustainability through resource recovery and energy efficiency by providing flexibility and renewable energy production (heat recovery, biogas, incineration, micro-hydropower, power to methane) in the system (Logan et al. 2021).

Wastewater may be used to extract energy, clean water, fertilisers, and nutrients, which can all be used to assist accomplish the SDGs. Best available methods (BATs) can help accelerate the transition to a circular economy by encouraging resource reuse and recovery and assuring long-term wastewater management. Another use of wastewater is direct and indirect potable reuse.

There are 48 countries in Asia, of which 37 are coastal states. These coastal countries can get non-conventional water resource from the desalination of sea water. Desalination has been an important water resource but brine management is another hurdle to procuring water from the sea. Brine is a saline wastewater produced by a variety of businesses (e.g., desalination, energy, and oil production) and its disposal has the potential to harm the environment. To solve this problem, brine treatment appears to be a potential solution for recovering additional freshwater and valuable elements like salts.

Technology is also evolving, bringing new choices for rural areas and communities, such as the usage of wetlands and lagoons, as well as decentralised or small-scale wastewater systems. Local standards should reflect local reality and authorities should consider local conditions when deciding between these possibilities.

Standards and rules must be redesigned for this changing urban setting, which may necessitate becoming more nuanced, holistic, dynamic, transparent, participatory, and contextual. Step wise incorporation of enforcement strategies to achieve compliance for water reuse should be planned (Schellenberg et al. 2020).

## 17.7 Conclusion

"Wastewater treatment not only reduces the problems linked to pollution but also resolves issues of water supply, environmental protection, health issues associated to water-borne diseases as population increase, industry, and urbanization." Wastewater can be used as a source of energy as well as repurposed in agriculture and industry, reducing the need for freshwater abstraction. Recognising wastewater as a resource decreases water pollution by avoiding tainted wastewater from being dumped into bodies of water. Reusing wastewater has two main benefits: it improves the living standards of the local population by generating economic opportunities and it saves money.

Innovations and extensive opportunities to use wastewater will become a necessity in the coming years of economic development. Many wastewater management methods and concepts have been successfully implemented in the past, but they have yet to reach their full potential. Not only is a paradigm shift in water policies and wastewater management required to protect human health, biodiversity, and ecosystems, but it is also necessary to modify our perception of wastewater as a valuable resource that may contribute to future water security.

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# Chapter 18
# Potential Role of Blue Carbon in Phytoremediation of Heavy Metals

**Sangita Agarwal, Prosenjit Pramanick, and Abhijit Mitra**

**Abstract** Man has come a long way from nomadic life to the present age through the corridor of technological advancement. In this transit, a wide range of anthropogenic activities have changed the homeostatic mechanism and disturbed the ecological balance. The various industrial processes, combustion of fossil fuels, agricultural activities along with natural processes distribute the heavy metals in the ecosystem, disperse in air, accumulate in water and soil impacting the health of the planet. Fe and Mn are essential as cofactors of various enzymatic reactions and required at low levels, higher concentration can be detrimental to health. Most other heavy metals are toxicants, they are non-biodegradable, bioaccumulate and biomagnify in higher trophic levels causing adverse effects. Coastal water often serves as the final destination of all wastes, in which heavy metals are important components. Hence there is a need to remediate the coastal and estuarine water in an economical manner. The various physical and chemical treatment processes of heavy metal removal from wastewater have many limitations so attention has shifted to methods which are economical and environmentally friendly like phytoremediation, wherein plants are used to eliminate the heavy metals. Phytoremediation includes phytoaccumulation, phytostabilization, phytodegradation, phytovolatilization and hydraulic control. In this article we have emphasized on the elimination of heavy metals from coastal water using endemic coastal vegetations that encompass mangroves and saltmarsh grass, collectively known as blue carbon.

**Keywords** Heavy metals · Coastal and estuarine water · Biopurification · Phytoremediation · Coastal vegetations

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## 18.1 Introduction

Blue carbon represents the special type of vegetation that thrive luxuriantly in the saline environment of estuaries, bays, seas and oceans. Mangroves, seagrass and several mangrove associate species are examples of blue carbon that are abundantly available in the coastal regions. The coastal waters are the most anthropogenically stressed habitat caused by the discharge of untreated waste from industries, aquaculture farms, tourism units, fish landing stations, trawlers and fishing vessels, etc.

The untreated wastes contain appreciable quantities of Zn, Cu, Mg, Fe, Co, Ni, Pb, Cr, Hg, etc. The heavy metals are considered as conservative wastes as they are not degraded by microbes. Heavy metals are compartmentalized and thus they remain either in dissolved state or deposited in sediment bed, depending on the physicochemical variables of the aquatic ecosystem especially salinity and pH. The heavy metals cause great concern due to their property of bioaccumulation, which is subsequently transferred to members of higher trophic levels and causes biomagnification. The coastal region of West Bengal especially the estuarine environment of Indian Sundarbans are regions of major anthropogenic stress because of several tourism units, fish landing stations, industries on the western bank of Hooghly estuary and shrimp farms. The heavy metals released from these sectors have deteriorated the estuarine alter to a great extent (Mitra 1998; Mitra et al. 1999, 2000, 2010; Bhattacharyya et al. 2001; Das et al. 2005; Barua et al. 2011; Mitra and Ghosh 2014; Banerjee et al. 2014).

With this background the present chapter aims to highlight the potential of selective blue carbon (mangroves and saltmarsh grass) in removal of toxic heavy metals (Cd, Cr, Pb and Hg) and upgrading the coastal water quality of West Bengal (Richter et al. 2016; Paz-Alberto et al. 2014).

## 18.2 Overview of Heavy Metals

### 18.2.1 *Definition and Sources*

Heavy metals are elements causing harm to ecosystem and all living beings (Appenroth 2010). They have high density in comparison to water (Fergusson 1990) with specific gravity and atomic weight more than 5 g/cm$^3$ and 40, respectively. Heavy metals originate not only from anthropogenic sources but also from natural sources. Volcanic eruption, forest fire, weathering of minerals and erosion are the significant natural sources of heavy metals in the environment. The major anthropogenic sources include mining, smelting, thermal power plants, foundries, dyes and pigments, fertilizer and pesticide industry, electroplating, tanneries, electrolysis, photography, aerospace and atomic energy sector, etc. (Modaihsh et al. 2004; Nagajyoti et al. 2010; Jaishankar et al. 2014) (Table 18.1). Rapid industrialization and urbanization have increased the heavy metal load in the ecosystem. In addition,

**Table 18.1** Sources of heavy metals in the environment

| Sources | Heavy metals |
|---|---|
| Volcanic eruption (natural) | As, Cd, Cu, Pb, Zn, Hg |
| Forest fire (natural) | Co, Mn, Cu, Pb, Ni, |
| Weathering (natural) | Cd, Pb, Ni, Zn, Cu |
| Mining | Cr, Ni, Mn, Cu, Zn, As, Pb, |
| Thermal power plants | Cd, Pb, As, Ni |
| Fertilizer and pesticide industry | As, Hg, Pb, Cd |
| Electroplating | Zn, Cd, Pb, Hg, Cr |
| Tanneries | Cr |
| Electrolysis | Zn, Hg |
| Aerospace | Pb |
| Atomic energy sector | Pb, Cr |

they are added to the water bodies through landfill leaching, acid rain, domestic effluents, agricultural run-off (Aksu and Kutsal 1990).

Heavy metals containing effluents are released into the water bodies, especially in developing countries which is a threat to aquatic life (Volesky 1990; Bishop 2002). Anthropogenic sources are categorized into (1) point sources (which are concentrated locally) and (2) non-point sources (which are diffused). Mining activities, metal based industrial operations and industrial effluents fall within the category of the former, while surface run-off from agricultural fields, urban areas, atmospheric pollution, etc. is under the latter.

The atmospheric emissions due to anthropogenic activities for many metals are higher in magnitude than natural discharges (Sposito and Page 1984). Heavy metals in the form of gas or particulates are dispersed to far-off places (many kilometres away) by wind and ultimately washed out from air into surface of water or land.

Heavy metals of anthropogenic origin are mostly discharged into the nearby rivers that freely find their way into the estuaries and coastal water bodies. Thus, coastal waters act as final receptacle of all categories of heavy metals and undergo ‘Speciation’ based on the salinity and pH of the aquatic phase (Horsfall and Spiff 2005). They ultimately get deposited on the sediment or body tissues of aquatic organism (bioaccumulation) or may remain in dissolved state.

Blue carbon plays a major role in bioaccumulation as they can assimilate toxic heavy metals from the ambient environment. The Indian Sundarbans receives heavy metals from various categories of industries located in the Haldia which is a port-cum industrial complex adjacent to the northwestern border of Indian Sundarbans.

### *18.2.2 Effects of Heavy Metals*

#### 18.2.2.1 Human Health

The heavy metals are known to induce widespread behavioural, biochemical and physiological changes in human beings (Jan et al. 2015). They affect various cell components and organelles such as mitochondria, lysosomes, nuclei and also the enzymes. The heavy metals interact with nuclear proteins and DNA, thereby damaging the DNA structure and leading to apoptosis or carcinogenesis (Tchounwou et al. 2012). They are also responsible for activating the signalling pathways (Valko et al. 2005). The heavy metal which shows maximum toxicity in living beings is Mercury and least is Aluminium (Pueyo et al. 2004; Filipiak-Szok et al. 2015).

#### 18.2.2.2 Ecosystem

The heavy metals when present in soil are taken up by the plants causing toxicity to both plants (Lokeshwari and Chandrappa 2006) and animals (Pandey and Madhuri 2014), by entering the food chain posing a negative impact on the ecosystem. Factors like polarity, vapour pressure, molecular stability and partition coefficient also impact the movement and distribution of pollutants. Heavy metals also modify the properties of soil like porosity, colour, pH, etc. which modifies the soil quality and further contaminates the water (Muchuweti et al. 2006; Masindi and Muedi 2018). The sediments accumulate the heavy metals while they are transported through the run-offs from various industries, villages, towns and cities. The toxicity of heavy metals is dependent on nature of heavy metals, their types, biological role, duration of exposure and organism which is exposed. The heavy metals make the organic pollutants less biodegradable, thereby doubling the polluting effect on the environment.

Saltmarsh grasses and mangroves, being sedentary in nature are constantly exposed to heavy metals during the tidal phases. Thus, they can be effective agents of phytoremediation in the coastal and estuarine regions.

## 18.3 Overview of Coastal Water and Blue Carbon

Coastal ecosystem is a zone of intersection between land and seawater. It lies at the lower end of the drainage basin. The coastal ecosystem comprises saline water, freshwater and brackish water (a mix of saline and freshwater) as well as coastlines and the adjacent lands. It is a residential complex of plants, aquatic animals and used as nursery for many fishes. This ecosystem encompasses mangroves, beds of mangrove associate species (seagrass, saltmarsh grass, etc.), sand dunes, mudflats, coral reefs, estuaries, etc. It provides various provisional services like raw materials (timber, leaves), food (fishes and other edible aquatic animals), medicinal ingredients (extracts of biomolecules from mangrove plants), resource of ornaments (like shells, pearls) and energy (originating from fuel of biomass and alcohol from Nypa palms) for the local communities.

Blue carbon plays a significant role in carbon sequestration being an important component of coastal vegetation. The sequestered carbon in mangroves, seagrass and saltmarsh grass is $168 \pm 36\text{gCm}^{-2}\,\text{yr}^{-1}$, $83 \pm 11\text{gCm}^{-2}\,\text{yr}^{-1}$, $242 \pm 26\,\text{gCm}^{-2}\,\text{yr}^{-1}$, respectively (Duarte et al. 2005; Breithaupt et al. 2012; Alongi 2012; Ouyang and Lee 2014) and mangrove ecosystem of Indian Sundarbans is a hotspot of carbon sequestration (Mitra and Zaman 2015; Mitra 2020).

The total coastal area covers more than 10% of the Earth surface which is around 3,56,000 km. It is under enormous anthropogenic stress because of the presence of industries, fishing and tourism units, etc. Moreover, excessive nutrients from agricultural and municipal run-off and other products used in households like cosmetics, drugs are all adding to the burden of the coastal pollution. Recreation and tourism sectors have developed along the coastal lines as the aesthetic beauty of nature is appealing and is a crowd puller.

The Indian coast, which covers a stretch of 7500 km, is characterized by varied landforms and ecosystems (https://incois.gov.in/portal/osf/osf.jsp). It consists of sandy beaches (43%), rocky areas (11%), mudflats and marshy wetlands (46%) with the two coastal plains (flattened land next to ocean), viz. (1) eastern coastal plain and (2) western coastal plain.

1. The *eastern coastal plain* is about 100–130 km long, which stretches from Eastern Ghat to Bay of Bengal and passes through the states of Odisha, Andhra Pradesh and West Bengal. Some major rivers form offshore sedimentary basins in this coastal part, namely Bengal, Mahanadi, Krishna-Godavari and Kaveri. The eastern coast is further divided into three categories, viz.

   (a) *Utkal coast*: It extends from Chilika Lake to Kolleru Lake and is characterized by heavy rainfall. Cultivation mainly consists of rice, coconut and banana in this coastal zone.
   (b) *Andhra coast*: It extends from Kolleru Lake to Pulicat Lake and forms a basin for the rivers of Krishna and Godavari.
   (c) *Coromandel coast*: It is lies between Pulicat Lake and Kanyakumari. In summer season, it remains dry and only receives rainwater during the winter season.

2. The *western coastal plain* is narrow with a width of 10–25 km and 1500 km and stretches from Gujarat in the west to Kerala in the south. It passes through the states of Gujarat, Maharashtra, Goa, Karnataka and Kerala. This is surrounded by caves, creeks and estuaries. The special character of western coastal plain is that the delta is not formed by flowing rivers. This coastal plain is economically very important. Fishing is the main occupation for coastal dwellers. In addition, international trading has developed through sea routes as many ports are located

along the coastal line. Western Coastal Plain is further divided into four categories, viz.

(a) *Kathiawar coast or Gujarat Coast*: This covers the whole Gujarat state which extends about 33,000 sq. km.
(b) *Konkan Coast or Maharashtra*: This rocky coast is narrow about 65 km near to Mumbai. The largest oil producing oilfields are present in this coastal area.
(c) *Goan Coast or Karnataka*: This is a sandy with rocky cliff coastal plain and is located in the Karnataka state.
(d) *Malabar Coast or Kerala*: This cost is lying between Mangalore to Kanyakumari and consists of lagoons which make this coast an important tourist spot.

The coastline of the state of West Bengal (about 158 km) is characterized by deltaic islands, estuaries, creeks, mudflats, sandy plains with beaches, dunes, geomorphic features and anthropogenic intrusion and therefore it is home to diverse species of flora and fauna (Bhattacharya et al. 2003). Sundarbans is a mangrove dominated deltaic complex situated at the apex of Bay of Bengal consisting of 102 islands and an area of 9630 sq. km (Mitra 2000). About 38% of the total Sundarbans area is part of India and remaining portion belongs to our neighbouring country Bangladesh. Indian Sundarbans is segregated into three parts, viz., eastern, western and central on the basis of the salinity profile. The southwestern part of Indian Sundarbans, known as Hooghly–Matla complex, is most useful for developing human inhabitants.

Medinipur coastal belt accounts for 27% of the state of West Bengal's coastal tract extending from New Digha on the west bank of Hooghly estuary to Junput, Dadanpatrabarh, Khejuri and finally to Haldia on the east and to the further northeast till Tamluk or to the bank of Rupnarayan river. Subarnarekha delta impacts the Medinipur coastal plain by depositing the bars into the sea. The shoreline of Medinipur coast consists of sand dunes, namely Contai, Digha, Paniparul, Ramnagar, Dariapur, Junput, Deuli, Uttar Darua. Casurina plant is mainly vegetated on the surface of Digha sand dunes, but they have been cut for urban development and sand dunes without these dune herbs and grasses move to inland and thus take the position in the paddy fields to the nearby villages of the coastal area. Hence, Digha dunes seem to be mobile.

## 18.4 Sources of Heavy Metals in Coastal Water Along the Bay of Bengal

According to WHO, coastal pollution implies introduction of substances indirectly or directly into the marine ecosystem harming living resources, marine life, causing health hazards to humans and hindering marine activities like fishing and other legitimate uses of the sea, impairing the quality of seawater. Coastal and marine water pollution has escalated in all the regions, primarily due to anthropogenic activities. Most of the pollutants entering the oceans and seas are emanating from land-based sources and comprises sand/silt, nutrients, toxic chemicals and oil. The marine life faces various threats which include waste deposition, contamination, exotic species, dredging, soil recovery, global climate change, overexploitation and harvesting.

The eastern coast of India (2545 km) mainly stretches from India–Bangladesh border in northeast to Kanyakumari in south, covering 21 districts of states like Tamil Nadu, West Bengal, Andhra Pradesh and Odisha. Rivers such as Ganga, Mahanadi, Brahmaputra, Krishna, Godavari, Kaveri, etc. drain into Bay of Bengal. The eastern coast is characterized by high temperature and medium rainfall (during June–September). The average salinity in Bay of Bengal is low due to the effects of dilution of the river systems and discharging of water (estimated at 71,645 $km^3$) into the Bay. Freshwater (~3000 $km^3$) is also added into Bay of Bengal from run-off and precipitation. The coastal area of Bay of Bengal is endowed with estuaries, brackish water, mangroves, coral reef and seaweed beds and thus it is very rich in flora and fauna.

The rapid growth of urbanization and industrialization with the uses of fertilizers, pesticides in the agricultural field is the primary sources of pollution in coastal areas of Bay of Bengal. The following are the sources from where a variety of pollutants enter into the Bay of Bengal:

### *18.4.1 Sewage Effluents*

Sewage means the domestic and industrial wastewater that enters seawater through the drains, rivers either in untreated or partially treated form. Along the coastal belt of Bay of Bengal, many factories such as pharmaceutical, textile mills, chemical plants, plastic, food processing, detergent, jute and tyre are present, from where the wastewater continuously goes (directly or indirectly) to the Bay of Bengal. Different types of pollutants like heavy metals, toxic chemicals, etc. are mixed with the aquatic environment, depleting the coastal resources, resulting in loss of biodiversity and risking public health Almost $1.11 \times 10^{10}$ $m^3$ sewage per annually enters into marine water from Indian coastal zone particularly from coastal cities and towns (Zingde 1999).

### *18.4.2 Land Run-Off*

Land run-off is another source of coastal pollution which mainly originates from urban and agricultural areas. As West Bengal is an agriculture-based state, farmers use different types of fertilizers, pesticides including organophosphates such as Malathion, Parathion, Diazinon and chlorinated hydrocarbons like DDT, BHC, Endrin and Dieldrin for rapid crop production and these chemicals flow through the canals, drain during flooding. Oil-like substances (emanating from cars, septic tanks) travel through flooded water and ultimately enter into coastal water.

### *18.4.3 Industrial Effluents*

Industrial and river run-off are the leading cause of pollution by heavy metals. Sediment is the store house of metals and thus the metal content in the sediment at the river mouth of Kaveri, Krishna, Ganga, Godavari and Mahanadi is higher than the inter-riverine coastal sediment. Among the heavy metals, zinc, copper, nickel, chromium, mercury, cadmium, cobalt, lead are predominantly present in the Bay of Bengal (BOBP 1994).

### *18.4.4 Antifouling Paints*

Antifouling paint is used to condition the fishing vessels, trawlers to prevent the growth of biofoulers like barnacles, oysters, etc. at the bottom and it is the source of Cu and Pb (Mitra 2013, 2019).

## 18.5 Phytoremediation

### *18.5.1 Definition*

Phytoremediation in simplest way can be defined as removing or remediating the toxicants from the environment by using plants. It is derived from Greek word 'phyto' meaning plant and 'remediation'—and 'remedium' which is Latin, meaning remove or correct an evil. Plants include grasses, trees as well as associated microbes are used to sequester, destroy, degrade, remove or stabilize hazardous chemicals from hydrosphere and lithosphere and using chemical, physical and biological processes (EPA US 2000; Erakhrumen and Agbontalor 2007; Moreno et al. 2008; Li et al. 2010).

The technique of phytoremediation is used to remove heavy metals, radionuclides and organic pollutants which include polynuclear aromatic hydrocarbons, pesticides, polychlorinated biphenyls. The plants while removing the pollutants do not disturb the topsoil and help to conserve fertility and utility of the soil. The organic matter input might help in improving the fertility of the soil too (Mench et al. 2009). This technique is efficient, eco-friendly, low cost and can be applied in-situ for removal of hazardous pollutants (Kawahigashi 2009; Saier and Trevors 2010; Kalve et al. 2011; Singh and Prasad 2011; Vithanage et al. 2012).

### *18.5.2 Mechanism of Phytoremediation*

The mechanism of phytoremediation may be discussed under seven broad ways, which include phytoaccumulation or phytoextraction, phytostabilization, phytofiltration, phytodegradation, phytovolatilization, phytodesalination and rhizodegradation (Alkorta et al. 2004) (Fig. 18.1).

#### **18.5.2.1 Phytoextraction**

Phytoabsorption, phytoaccumulation or phytosequestration all refer to the technique of phytoextraction, in which the roots of plant take up the contaminants either from water or soil that gets translocated either to shoot system or to the aboveground biomass where they are stored (Sekara et al. 2005; Yoon et al. 2006; Rafati et al. 2011). The translocation of metal toxicants to the shoot plays a significant role in effective phytoextraction as the feasibility of extraction from the root biomass is quite low (Zacchini et al. 2009; Tangahu et al. 2011). Thus, the value of translocation factor is a determining factor in order to evaluate the phyto-extracting potential of a floral species.

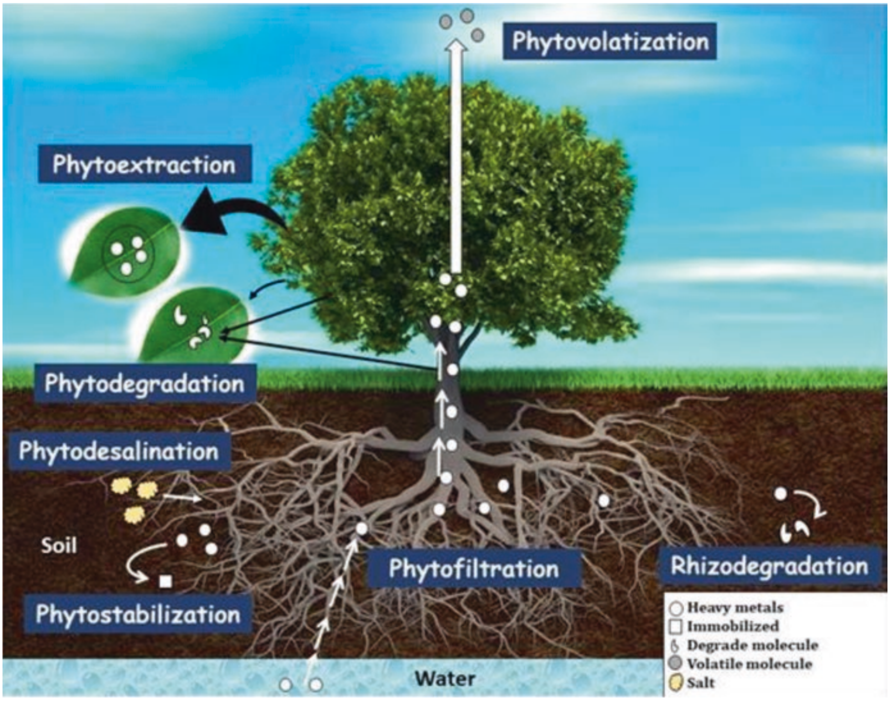

**Fig. 18.1** The mechanisms of heavy metals uptake by plant

#### 18.5.2.2 Phytofiltration

The technique of removing the pollutants from untreated wastewater or surface water by plants is called phytofiltration (Mukhopadhyay and Maiti 2010). In this technique roots of the plant or seedlings or excised shoots can be used which is known as rhizofiltration or blastofiltration or caulofiltration, respectively, depending on the part of the plant used (Mesjasz-Przybylowicz et al. 2004). The motility of contaminants in the untreated water is minimized by phytofiltration as the contaminants are adsorbed or absorbed by the plant from contaminated surface water or wastewater.

#### 18.5.2.3 Phytostabilization

In the technique of phytoimmobilization or phytostabilization, specific varieties of plants species are used which immobilize the toxicants present in soil by precipitation, complexation, sorption through roots or reduction of valency of metals in rhizosphere (Yoon et al. 2006; Ghosh and Singh 2005; Wuana and Okieimen 2011). The toxicity of metals varies with their oxidation state as, for example, the toxicity and mobility of hexavalent chromium Cr (VI) are more than the trivalent chromium Cr (III) (Wu et al. 2010), so by excretion of special enzymes like reductase and oxidase, the plants convert the more toxic form of the metals to lesser ones. Thus, by immobilization the mobility and bioavailability are reduced and leaching to underground water is prevented as well as their entry to the food chain is also substantially blocked (Erakhrumen 2007).

#### 18.5.2.4 Phytovolatilization

As the name suggests, the technique of phytovolatilization implies uptake of pollutant by plants and their conversion to a volatile form and released in the air. This technique can be useful in removing metals like mercury, selenium and organic pollutants. Since the toxicants are not completely removed and transferred from one component of environment to other, phytovolatilization has limited application (Padmavathiamma and Li 2007).

#### 18.5.2.5 Phytodegradation

In phytodegradation the enzymes like oxygenase and dehalogenase are used by plants to degrade the organic pollutants and are independent of the rhizospheric microorganisms (Vishnoi and Srivastava 2008). The green plants are acting as 'Green Liver' of biosphere as they are detoxifying the accumulated organic xenobiotics from contaminated environment by their metabolic processes. This technique application is limited to pollutants which are biodegradable and hence cannot be used for elimination of metal toxicants.

#### 18.5.2.6 Rhizodegradation

The use of microorganism to degrade the organic pollutants present in the soil in the rhizosphere is termed as rhizodegradation (Mukhopadhyay and Maiti 2010). The area around the roots (1 mm) of the plant is rhizosphere and is controlled by the plants (Pilon-Smits 2005). The microbial activity in the rhizosphere is 10 to 100 times higher due to secretion of certain enzymes, carbohydrates, flavonoids and amino acids which create nutrient rich environment for breakdown of organic pollutants and stimulate the activity of microbes (Kuiper et al. 2004; Yadav et al. 2010).

#### 18.5.2.7 Phytodesalination

Phytodesalination is the technique of removing salts by using halophytes (Manousaki and Kalogerakis 2011; Zorrig et al. 2012; Sakai et al. 2012). The halophytes are better suited and adapted to take up heavy metals in comparison to the glycophytic plants (Manousaki and Kalogerakis 2011). The use of halophytes would be discussed in detail in the following section with special emphasis on the coastal belt of West Bengal (Niyogi et al. 1997).

### *18.5.3 Selection of Plant Species*

The selection of plants for phytoextraction should take into account the following factors (Tong et al. 2004; Sakakibara et al. 2011; Shabani and Sayadi 2012), namely

- The growth rate of plants should be significant having easy harvesting and cultivation potential.
- The aboveground biomass should be more with highly branched and well distributed root system.
- Plants should be able to adapt to the existing environmental conditions, tolerate the toxic effects of heavy metals and absorb targeted toxicants from soil and translocate to the shoot system. They should also show resistance to pests and pathogens.
- They also should be repulsive to the herbivores so as to avoid contamination to the food chain.

There are two approaches used in determining the potential of plant in phytoextraction such as concentration of heavy metal in shoot and biomass of shoot (Li et al. 2010). First approach is use of hyperaccumulators that accumulate target toxicants to larger extent but aboveground mass is less comparatively. Second, selected plants like Indian mustard accumulate lesser quantity of heavy metals but aboveground biomass is relatively more, so overall accumulation is similar to hyperaccumulators as more biomass is produced (Tlustoš et al. 2006). According to some workers hyperaccumulators produce low-volume biomass, are metal rich, economical, easier to handle and better for safe disposal as well as metal recovery (Chaney et al. 2007). Grasses are preferable compared to trees or shrubs because of higher growth rate, biomass and better capability of adaption to stress (Xia 2004; Malik et al. 2010). The food crops are not preferred for phytoextraction of heavy metals because they run a risk of contaminating the food chain (Vamerali et al. 2010).

### *18.5.4 Factors Affecting Phytoremediation*

The uptake of heavy metals by plants is dependent on a number of factors and understanding of these determinants can help in improving the performance of these plants (Fig. 18.2). The characteristics of plant species are major determinant in uptake of compounds and thus species having greater remediation efficiency is selected as they can hyperaccumulate (Burken and Schnoor 1996; Prasad and De

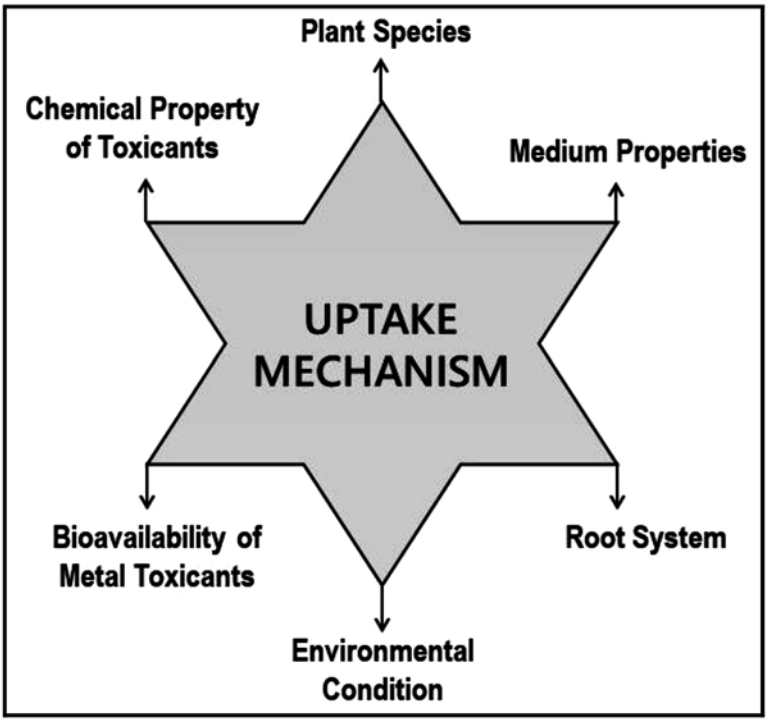

**Fig. 18.2** Factors which effect the uptake of heavy metals by plants

Oliveira Freitas 2003). The medium properties and agronomical properties influence remediation. The root systems play an important role in phytoremediation as they absorb contaminants, metabolize or store inside the plant tissue. Various enzymes released from plant roots also degrade the contaminants present in the soil which can serve as another mechanism of phytoremediation. The roots adapt morphologically to the environmental conditions such as in response to drought they increase the root diameter (Merkl et al. 2005). The environmental conditions also influence the vegetative uptake (Burken and Schnoor 1996). The root length is often affected by the temperature. Some plants are selective in absorbing one specific contaminant in greater concentration than others. The uptake of metals by plants is dependent on the bioavailability of metal in aquatic phase, which is further dependent on interaction of the specific metal with other substances and elements also its retention time in water. The addition of ligand changes the leaching potential below root system through formation of ligand–metal complex affecting the bio-uptake of heavy metals (Seuntjens et al. 2004).

## 18.6 Uptake of Heavy Metals by Coastal Vegetation

### *18.6.1 Mangroves*

Mangroves are a group of plants that grow in the intertidal zone of tropical and subtropical regions of the coastal area. They are salt tolerant with broad leathery and evergreen leaves. A special type of root is grown from the main stem and branches towards down and helps in the support of the tree in the muddy area (Fig. 18.3). They act as a barrier between land and sea and absorb the force of sea wave.

Indian Sundarbans is the survival ground of mangrove forest. About 34 true mangrove species are present in this region (Chaudhuri and Choudhury 1994) and the dominant species in almost all the islands are *Avicennia alba*, *Sonneratia apetala*, *Avicennia officinalis*, *Avicennia marina*, *Excoecaria agallocha*.

One of the indicators for monitoring the coastal heavy metals pollution is accumulation of heavy metals in mangrove species (Saenger and McConchie 2004). The sediment of the mangrove forest has more potential to store heavy metals than the ambient water (Kamaruzzaman et al. 2008) due to their unique physicochemical properties (Qiu et al. 2011). The sediments are primarily anaerobic, containing high amount of organic matter, which helps in the storage of heavy metals (Tam and Wong 2000) and through the sediments heavy metals are transferred to the trees of mangrove species (Defew et al. 2005). A case study on the *Avicennia marina* in Qeshm Island showed that various vegetative parts (root, stem, leaf) are good bioindicators for different metals (Einollahipeer et al. 2013).

Scientists showed that mangroves can accumulate the metals from the sediment and store into their tissue cells and thus remove the pollutants from the ambient media (MacFarlane et al. 2007). In this way, mangroves can serve as an important member in natural wastewater treatment system and also in the phytoremediation process (Sodré et al. 2013; Tansel et al. 2013; Ouyang and Guo 2016). Other researchers have also shown that mangroves have the potential to assist in phytoremediation of coastal soil (Nath et al. 2014; Chai et al. 2018).

### 18.6.2 Saltmarsh Grass

Saltmarsh grass is a group of floral species that is characterized by low succulent herbs, salt tolerant and sedges. They are mostly found in intertidal zone of the coastal area where they help in the inundation of marine tides. They provide some ecosystem services like maintenance of coastal water quality, flood and storm surge protection as well as shoreline stabilization and also used as habitat for fish, shellfish and wading birds, etc. (Costanza et al. 2008; Gedan et al. 2011). Depending on the nature of the saltmarsh soil, they act as a source or sink of carbon dioxide (Khan 2016). They accumulate organic matter from the sediment and also resist the erosion from waves and storm surges.

*Porteresia coarctata* is a dominant saltmarsh grass species (Fig. 18.4) in mangrove dominated Indian Sundarbans and considered as a pioneer species for its island ecological succession (Mitra 2013). It has a tetrapod (2*n* = 48) structure and found as mangrove associate species in intertidal mudflats, where soil is submerged with seawater for twice a day and sometimes for a long period (Flowers et al. 1990).

**Fig. 18.3** Mangroves with special type of root system

**Fig. 18.4** Dominant saltmarsh grass *Porteresia coarctata* along the coastal Bay of Bengal

Effluents from industries, domestic wastes, agricultural run-off infiltrate the coastal zone and contaminate the saltmarsh sediments with halogenated hydrocarbons and heavy metals. These metals are accumulated in the saltmarsh tissues. A study was undertaken to determine the potential of *P*. *coarctata* in accumulating the selective heavy metals (Cu, Pb, Zn) at three sites of Indian Sundarbans (Banerjee et al. 2014). It is important to note that the proximity of Indian Sundarbans to highly populated city of Howrah, Kolkata and Haldia makes the region susceptible to anthropogenic stress. The results of the study showed that selective heavy metals accumulated in *P. coarctata* and the dry weight concentration of Zn, Cu and Pb ranged from 68.17 ± 12.11 to 118.46 ± 30.22 ppm, 27.53 ± 4.36 to 45.66 ± 9.87 ppm and 5.49 ± 1.91 to 15.04 ± 3.31 ppm, respectively (Banerjee et al. 2014). Thus *P. coarctata* can be used in phytoremediation to treat contaminated effluents.

## 18.7 Conclusion

Coastal regions are treated as bins of modern civilization hence wastes of all categories are drained into the system that contain significant quantity of heavy metals. The coastal areas of West Bengal are no exception to the rule due to presence of tourism units, industries, fishing vessels and trawlers, aquaculture farms and fish landing stations. In most cases the waste released from these units are not even partially treated and hence the environment of coasts gets deteriorated. Blue carbon which includes mangroves and saltmarsh grass acts as potential sink of heavy metals. The heavy metals accumulate in their body tissue as a function of salinity, pH and concentration of metals in the ambient media. Mass plantation of mangroves can bioaccumulate heavy metals in their vegetative parts, which can be later used as timber. Saltmarsh grass is highly effective to control erosion in coastal regions and hence their propagation can provide ecosystem services preferably regulating services by way of phytoremediation and erosion control. Finally, assessment of physicochemical variables in different tidal phases needs to be carried out for biomonitoring heavy metals in the body tissues of resident species.

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# Chapter 19
# Biodegradation Potentials of Cassava Wastewater by Indigenous Microorganisms

**Sylvester Chibueze Izah, Glory Richard, Tamaraukepreye Catherine Odubo, and Ayobami Omozemoje Aigberua**

**Abstract** Many microorganisms tend to remove environmental contaminants (non-toxic and toxic) or degrade organic compounds. There are different techniques for eliminating toxicants or enhancing the degradation of organic substrates. The choice of technology depends on the type and physical condition of the materials or substrates being degraded. While Nigeria is the largest producer of cassava in the world, accounting for approximately 20% of global output it is not without some adverse environmental implications. During the processing of cassava into *garri* (cassava flakes), large volumes of under-utilized effluents are generated in processing mills, especially in developing countries like Nigeria. Consequently, cassava wastewater poses public environmental trepidation in processing communities or areas. These effluents are acted upon by indigenous and opportunistic microbes, thereby resulting in the fouling of air, as well as altering the physicochemical characteristics of the effluents and their receiving environment. Fungi (moulds and yeasts) and bacteria (*Acetobacter*, *Bacillus*, *Micrococcus*, *Lactobacillus*, *Corynebacterium*, *Pseudomonas*, *Staphylococcus*, *Aspergillus* and *Penicillium* species and *Saccharomyces cerevisiae*) have been reported to effectively degrade cassava wastewater. These microbes possess the ability to reduce the level of biological and chemical oxygen demands, nutrients (phosphate, nitrate and sulphate), conductivity, total dissolved solids, salinity and some trace metals. The biodegradation of cassava wastewater can be influenced by several factors, including temperature, pH,

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nutrients, oxygen, biodegradability potentials, photo-oxidation, bioavailability, among others.

**Keywords** Applied microbiology · Cassava wastewater · Environmental health · Public environmental trepidation

## 19.1 Introduction

Many microorganisms, especially the ones that can thrive and adapt to the soil environment, have the potential to transform or degrade some environmental contaminants into non-toxic or less toxic forms. Microorganisms that possess these tendencies have been widely utilized for the remediation of hydrocarbons associated with crude oil (Chukwura et al. 2016). Microorganisms are used for exterminating contaminants from the environment. This is because their deployment is less expensive compared to surfactants and dispersants that are used to remediate polluted hydrocarbon sites. Some of these microorganisms with a tendency to utilize hydrocarbons and its derivatives include *Aspergillus niger*, *Aspergillus fumigatus*, *Penicillium xingjiangense*, *Mucor racemosus* and *Rhodotorula* sp. (Chukwura et al. 2016), *Escherichia fergusonii*, *Klebsiella variicola* and *Micrococcus luteus* (Nwankwegu et al. 2016). This further suggests that both bacteria and fungi can be conveniently used to degrade hydrocarbons originating from crude oil in the environment (Chukwura et al. 2016). Studies have shown that fungi have a higher tolerance to the toxicity of hydrocarbons because of their physiology and adaptation strategies. As such, they possess mechanisms that aid the removal of environmental contaminants (Chukwura et al. 2016).

During the degradation of hydrocarbon-related materials, several factors have been reported to influence the process. These factors include biological, physical and chemical characteristics of the substances that are being degraded, as well as the degrading medium (Singh et al. 2017). Chukwura et al. (2016), Ojo (2005) reported that temperature, nutrients, oxygen, biodegradability potentials, photo-oxidation, bioavailability, soil moisture, soil acidity and alkalinity could influence biodegradation processes in soil medium.

Apart from the microbial degradability of crude oil, microbes, especially fungi, have demonstrated the potential to utilize industrial and food processing wastewaters as sources of carbon and energy (Izah et al. 2017a, b). Some of the food processing wastewaters that have been degraded by microbes include tannery effluents (Okoduwa et al. 2017), palm oil mill effluents (Iwuagwu and Ugwuanyi 2014), pharmaceutical effluents (Abioye et al. 2015), textile effluents (Abioye et al. 2014) and cassava wastewater (Izah et al. 2017a, b).

Cassava is a major tuber and carbohydrate crop that is consumed in many regions of the world. As such, it is a staple food just like rice, maize, etc., across many countries in West Africa. It is consumed by over 2 billion people globally (Ukwuru and Egbonu 2013). Of these, over 500 million consumers reside in developing nations

(Kamalu 1995), with about 300 million living in tropical countries (Eze and Onyilide 2015). The primary nutritional composition of cassava, especially carbohydrates and vitamins, is determined by the maturation (age) of the crop, soil characteristics and species type. Cassava is cultivated in many regions of the world. This is possibly due to the fact that it can tolerate several adverse environmental conditions. Usually, the crop is harvested between 7 and 13 months after planting, although this largely depends on the variety (Ezeigbo et al. 2014).

As of 2017, the global cassava production statistics was 291,992,646 tonnes. Of these, Nigeria, Congo Democratic Republic, Thailand, Indonesia, Brazil, China, Angola, Cambodia, Vietnam, Mozambique, Cote D'Ivore, Tanzania, Malawi, China, Sierra Leone, Benin Republic, India and Paraguay account for 20.37%, 10.82%, 10.61%, 6.52%, 6.46%, 6.33% 4.02%, 3.62%, 3.52%, 3.00%, 1.99%, 1.84%, 1.72%, 1.70%, 1.67%, 1.63%, 1.49, 1.43% and 1.08%, respectively (Tilasto 2021), with other nations accounting for 10.08% of cassava production in tonnes. Nigeria is the leading cassava producer in the world and it has dominated the sector for over 10 years (Izah and Aigberua 2017; Izah et al. 2017a, b, c, d, e, f, g, h, 2018a, b, 2019a, b; Izah 2018a, b, c, d, 2019a). However, Nigeria's cassava production is dominated by smallholders that use rudimentary equipment for processing.

During the transformation of cassava to processed cassava flakes, popularly known as gari, large volumes of wastewater are generated. However, these effluents are poorly managed in the processing mills. They are discharged into nearby pits and bush covers around the processing mills (Fig. 19.1). Sometimes, the effluents flow into major roads and living quarters from where they cause attendant environmental pollution, including foul odour, impact on biodiversity and changes in the microbial and physicochemical characteristics of the receiving environment (soil and water).

Due to the ubiquitous nature of microorganisms, especially bacteria and fungi, as well as their ability to thrive and adapt to the diverse environment, many microbes

**Fig. 19.1** A typical cassava wastewater contaminated soil

that are found in cassava wastewater and soils contaminated by cassava mill effluents are known to biodegrade hydrocarbons. Therefore, the focus of this study is to investigate the biodegradation potentials of cassava wastewater by indigenous microorganisms that colonize it. The findings from this study will help in identifying the microbes with high degradation potentials. The findings will also be helpful to environmentalists and individuals who seek alternative treatment techniques for agro-waste waters. In addition, results from this study will aid better decision making for effective management of cassava wastewaters.

## 19.2 Characteristics of Cassava Wastewater

Globally, cassava processing industries cause environmental pollution from the large volumes of water produced during the processing of cassava into gari. The released effluent is highly toxic and rich in organic materials that cause severe threats to the environment and aquatic life forms in recipient water bodies (Kandasamy et al. 2015). Cassava wastewater characteristics are often classified into three groups, viz.: biological, chemical and physical. However, most authors often report the physical and chemical characteristics as physicochemical characteristics, while the most commonly studied biological parameters of cassava mill effluents are the microbial characteristics.

The commonly reported physicochemical characteristics of cassava wastewater include turbidity, taste, colour, odour, pH, total suspended solids, total hardness, total alkalinity, salinity, electrical conductivity, cyanide, nitrate, nitrite, sulphate, calcium, sodium, magnesium, potassium, carbonates, dissolved oxygen, chemical and biological oxygen demands and heavy metals (iron, manganese, zinc, copper, cadmium, chromium, lead, silver, mercury, etc.) (Izah 2019a, b; Izah et al. 2017a, b, 2019a; Orhue et al. 2014; Rim-Rukeh 2012; Adejumo and Ola 2011; Ehiagbonare et al. 2009; Enerijiofi and Chukwuma 2018; Enerijiofi et al. 2017; Patrick et al. 2011; Olorunfemi and Lolodi 2011; Omomowo et al. 2015; Agwaranze et al. 2018).

Furthermore, most of these studies have indicated that the physicochemical characteristics of cassava wastewater often exceed the recommended limit for effluent discharge into the environment as specified by Federal Environmental Protection Agency, Nigeria (FEPA 1991) as cited by Izah et al. (2017a), Enerijiofi and Chukwuma (2018) and Enerijiofi et al. (2017). The effects of cassava wastewater on the physicochemical properties of recipient water and soil have been comprehensively reported in literature (Izah et al. 2017c; Ehiagbonare et al. 2009; Patrick et al. 2011; Okechi et al. 2012; Osakwe 2012; Eneje and Ifenkwe 2012; Chinyere et al. 2013, 2016; Okpamen et al. 2014; Okunade and Adekalu 2014; Orhue et al. 2014; Ezeigbo et al. 2014; Ibe et al. 2014; Igbinosa and Igiehon 2015). Apart from the physicochemical characteristics that are common to both water and soil, other properties that are peculiar to soil include soil particle size and structure (% sand, silt and clay, porosity, bulk density).

Cassava wastewaters have been reported to depict a tendency to alter the characteristics of receiving water resources (Okunade and Adekalu 2013; Afuye and Mogaji 2015; Omotioma et al. 2013; Oghenejoboh 2015; Nwaugo et al. 2007), causing some of the recipient water characteristics or constituents to exceed regulatory limits specified by the Standard Organization of Nigeria. Some of the major physicochemical characteristics of wastewater are vital. For instance, the chemical and biochemical oxygen demand determines the strength of organic contents and wastewater biodegradability (Lawal et al. 2019). Furthermore, Olaoye et al. (2018), Izah et al. (2017a, b, f) reported that dissolved oxygen, biochemical and chemical oxygen demand, cyanide, heavy metals and suspended matter are among the significant pollution determinants of cassava wastewater.

Different microbial groups (densities and isolates) have been reported in cassava mill effluents and contaminated environments (soil and surface water). Microbes have been reported to be ubiquitous mainly due to their ability to survive under different environmental conditions, whether favourable or unfavourable. The characteristics of cassava mill effluents include the group of microbes that are found in the wastewater. For instance, cassava wastewater is known to be acidic (Izah and Ohimain 2015), containing cyanide (Izah et al. 2017f) and other nutrients.

The common groups of microorganisms that have been reported in cassava mill effluents include *Neisseria*, *Streptococcus*, *Staphylococcus*, *Bacillus*, *Enterobacter*, *Proteus*, *Lactobacillus*, *Pseudomonas*, *Micrococcus*, *Saccharomyces*, *Penicillium*, *Aspergillus* and *Mucor* (Izah et al. 2018b).

At the point of discharge of cassava wastewater into surface water bodies, *Alcaligenes*, *Flavobacterium*, *Pseudomonas*, *Micrococcus*, *Candida*, *Penicillium*, *Aspergillus*, *Geotrichum* and *Saccharomyces* species have been recorded (Omotioma et al. 2013; Nwaugo et al. 2007; Izah et al. 2018b). Some other authors reported *Flavobacterium*, *Micrococcus*, *Pseudomonas*, *Aspergillus*, *Mucor* species, *Penicillium oxialicum; Penicillium notatum*, *Saccharomyces cerevisiae* in cassava wastewater (Ehiagbonare et al. 2009; Rim-Rukeh 2012). Also, microbes such as *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas*, *Bacillus*, *Micrococcus*, *Proteus* and *Enterobacter* species and *Saccharomyces cerevisiae*, *Aspergillus*, *Mucor*, *Penicillium* and *Rhizopus* species have been reported in cassava mill effluents contaminated soil (Izah and Aigberua 2017; Igbinosa and Igiehon 2015; Ezeigbo et al. 2014; Okechi et al. 2012; Eze and Onyilide 2015). The microbes that have been reported in cassava processing wastewater and contaminated soil are opportunistic pathogens. This implies that these microbes are environmental contaminants.

## 19.3 Environmental Impacts of Cassava Wastewater

Cassava production in Nigeria is dominated by smallholder processors who utilize rudimentary equipment for processing. The schematics for gari production from cassava tubers are shown in Fig. 19.2. However, there are slight variations in the

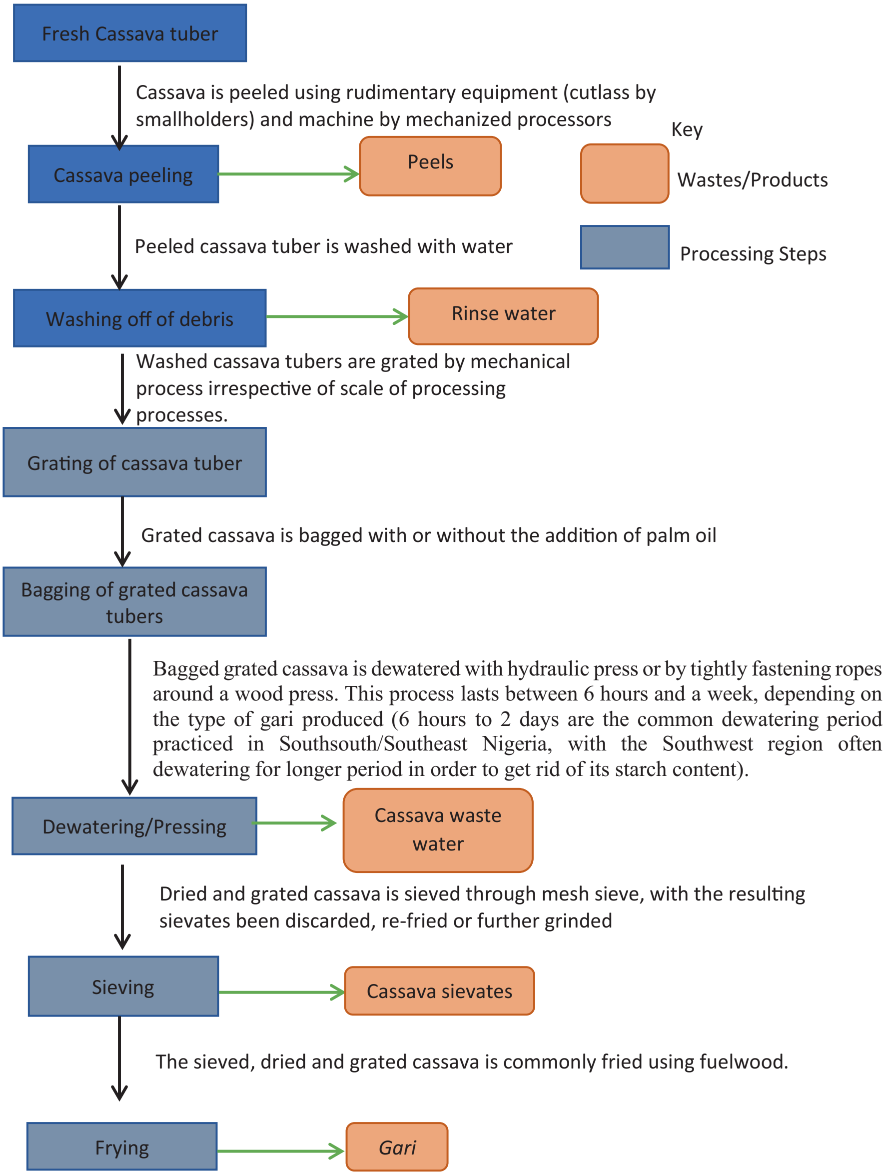

**Fig. 19.2** Schematics of gari production from cassava tuber by smallholder processors in Nigeria (CME = cassava mill effluents); adapted from Izah 2016, 2018c, 2019b

production process among ethnic groups in Nigeria, especially in the southwestern and southeastern regions.

During the production of cassava into flakes (popularly known as gari), large wastewater are generated. In the largest cassava producing nation, the number of cassava tubers and amount of wastewater generated during processing have been

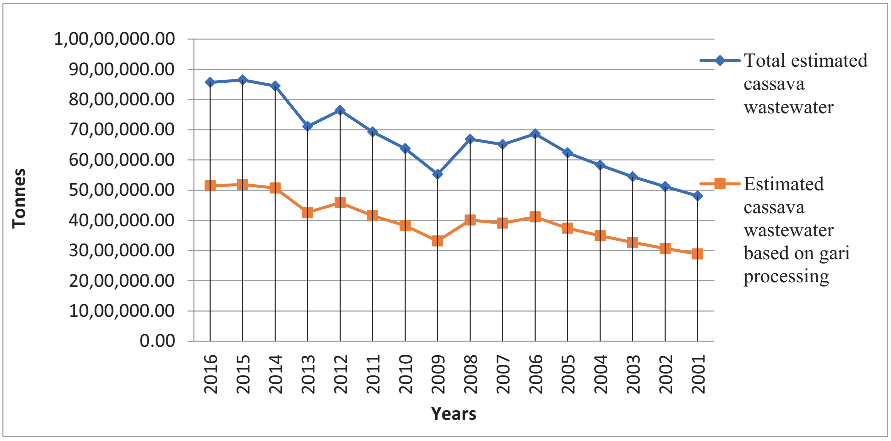

**Fig. 19.3** Estimated quantity of cassava wastewater produced under Nigerian setting between 2001 and 2016 (Izah 2018c)

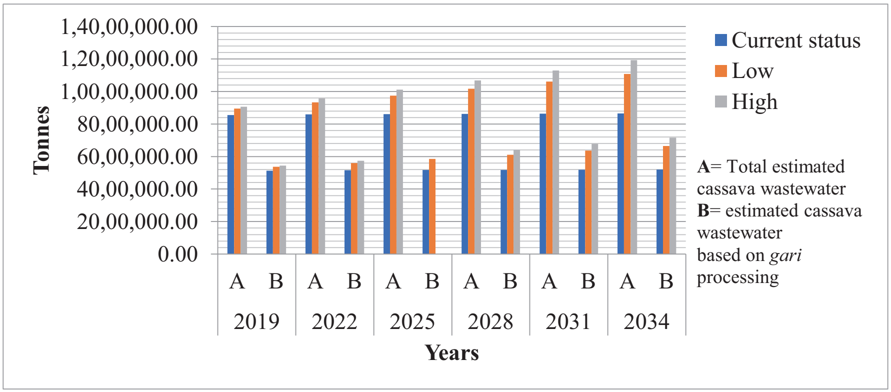

**Fig. 19.4** Projected quantity of cassava wastewater produced under Nigerian setting between 2019 and 2034. Adapted from Izah (2018c)

estimated (based on the quantity of cassava mill effluents resulting from gari processing) (Izah 2018c) (Fig. 19.3). Also, projections have been made under three scenarios at 3-year intervals from 2019 to 2034. The scenarios were considered based on 0.17%, 4.37% and 5.67% growth rate based on average production of 2014–2016 for a current, average production of 2013–2016 for low and average production of 2012–2016 for high growth rate, respectively (Izah 2018c). The resulting quantity of cassava mill effluents generated under the different scenarios is presented in Fig. 19.4.

Due to the dominance of the sector by smallholder processors, it is difficult to gather all the effluents generated for reuse in biotechnological advances. As such, Izah (2018c) estimated that about 45.0–65.0% of the cassava wastewater generated in Nigeria could be obtained and utilized for biotechnological innovations.

In Nigeria, cassava wastewaters are often indiscriminately discharged into the environment with little or no treatment. Cassava wastewater has been reported to alter ambient environmental conditions (especially soil, water and air) and affect biotic species in environmental matrices (soil and surface water) (Izah et al. 2018b). The alteration caused by cassava mill effluents is associated with the adverse changes in physicochemical and biological characteristics of wastewater.

Studies have shown that cassava wastewater depicts low pH (high acidity), cyanide, total suspended solids and total solids. Other parameters of cassava wastewater that often exceeds the allowable limits for wastewater discharge include heavy metals, oxygen-related parameters (chemical and biochemical oxygen demands and dissolved oxygen), conductivity, anions (sulphate, nitrate and phosphate), Izah et al. 2017a, b. Different groups of microbial diversity (total bacterial load, total coliform, faecal coliform, *E. coli*, *Staphylococci* counts, total fungi, lipolytic bacteria, cellulolytic bacteria, phosphate solubilizing bacteria and nitrifying bacteria) and related enzymatic parameters (acid phosphatase, alkaline phosphatase, dehydrogenase, lipase, urease, cellulose) have been reported in cassava mill effluents contaminated environment (Izah et al. 2018b).

Generally, cassava wastewater produces a strong foul or offensive odour that can be perceived as far as 90.3 to 102.3 m from its source (Ehiagbonare et al. 2009). The odour worsens during the degradation of wastewater by indigenous microbes in the cassava mill effluent contaminated environment. Studies have shown that cassava wastewater could negatively impact community pride due to the resulting offensive odour emanating from the discharged effluents (Ero and Okponmwense 2018). The authors opined that the odour interferes with human relations, leading to unhealthy annoyance, breathing and sleeping difficulties, eye, nose and throat irritations while also discouraging capital investment and leading to slow developmental growth in such communities (Derek 1992; Ero and Okponmwense 2018). In addition, the saturation of fouled air in a cassava processing vicinity may exacerbate breathing problems due to the inhalation of cyanide from the milling process.

Cyanide is very toxic to humans. According to Uhegbu et al. (2012), when cyanide combines with gases such as carbon monoxide, hydrogen sulphide and azide, they could hinder cytochrome oxidase activities, thereby interfering with mitochondrial oxidation and phosphorylation processes which ultimately inhibits energy formation in the form of ATP. These gases, such as carbon monoxide and hydrogen sulphide, have been reported in communities that produce higher quantities of gari in the Niger Delta region of Nigeria (Richard et al. 2019).

In soil, cassava wastewater could alter the characteristics of recipient soil, thereby rendering the soil devoid of vegetation. The presence of cassava wastewater in soil could negatively affect the growth and productivity of certain plants (Nwakaudu et al. 2012). Cassava mill effluents have the tendency to alter the physiological responses of domestic animals, sheep and goats, but does not affect cats, fowls and pigs (Ero and Okponmwense 2018; Ehiagbonare et al. 2009). The toxicity of cassava wastewater can be attributed to its acidity and cyanide composition.

Some food crops such as *Dioscorea dumetorum* (domestic yam), *Dioscorea dumetorum* (wild yam), *Dioscorea rotundata (*white yam), *Dioscorea alata* (water yam), *Xanthosoma sagittifolium* (red cocoyam), *Colocasia esculenta* (white cocoyam), *Ipomea batatas* (red sweet potato), *Ipomea batatas* (white sweet potato) have been reported to absorb contaminants from soil (Uhegbu et al. 2012). Hence, cassava wastewater in agricultural fields is a source of concern. This is because cyanide could cause several health issues in humans over a prolonged period of time, depending on the exposure concentration. According to Uhegbu et al. (2012), cyanide could lead to hyperventilation, headache, collapse and coma, nausea and vomiting, generalized weakness, respiratory distress while also affecting animals such as insects. Cyanide has been reported to affect insects such as *Malacosoma americanum*, an eastern tent caterpillar (Uhegbu et al. 2012).

In water, cassava mill effluents can alter the characteristics of the receiving water body. The notable water parameters that are altered by cassava wastewater include pH, dissolved solids, oxygen-related parameters, hardness, anions and cations nutrients, heavy metals, cyanide, colour, alkalinity, etc. (Izah et al. 2018b). In surface water, cassava mill effluents could lead to eutrophication, possibly due to high nutrient content (nitrification). Also, these effluents have been widely reported to induce toxicological responses in fishes. Some of the effects of cassava processing wastewaters on fish mortality (Seiyaboh and Izah 2018; Asogwa et al. 2015; Adeyemo 2005), behavioural responses (Asogwa et al. 2015; Adeyemo 2005), haematological, histopathological effects (Adeyemo 2005), enzymatic effects (Asogwa et al. 2015), have been reported. These effects are associated with the acidity and cyanide composition of cassava wastewater. Just like in soil, wastewater could alter the microbial characteristics of water resources. The authors have reported that cassava mill effluent lowers the density and diversity of microorganisms in receiving environments (Izah and Aigberua 2017; Izah et al. 2018b). This may ultimately lower the role of the microbes in the receiving environment, especially soil.

## 19.4 Concept of Biotechnology

Biodegradation is generally defined as the process by which organic substances are broken down into more minor compounds by microorganisms. More generally, it is the change in any substrate mediated by biological agents (Marinescu et al. 2009; Bennet et al. 2002). Complete mineralization can be achieved through the growth of the organism using the contaminant as a source of carbon and energy or by co-metabolism in the presence of a growth factor (Fritsche and Hofrichter 2001). Biodegradation is carried out by a huge assortment of life forms comprising mainly bacteria, fungi, algae, protozoa and possibly other life forms. And these organisms have the capability and metabolic machinery to break down, transform or accumulate a large variety of compounds, including crude oil (hydrocarbons), polychlorinated biphenyls (PCBs), phenols and their derivatives, heavy metals, wastewaters, etc. (Leitão 2009). The term biodegradation is now commonly used in relation to waste management, ecology, biomedicine and environmental remediation (bioremediation). For example, bioremediation of soils contaminated with petroleum hydrocarbons has been known to be effective, economical and more environmentally friendly as compared with conventional methods (Marinescu et al. 2009).

However, biotechnology has proven to have the potential to contribute immensely towards the development of sustainable and more affordable treatment of these hazardous wastes. Microorganisms have proven to be effective in breaking down these environmental contaminants into less toxic substances; thus, microbes could be considered nature's way of recycling wastes. There is no waste in nature as almost everything gets recycled and the secondary metabolites formed or products from one organism can even become sources of carbon and energy for others which further encourages the degradation process until complete mineralization is achieved with usually the formation of carbon dioxide, mineral salts and water (Pramila et al. 2012; Joutey et al. 2013).

The use of bioremediation as a biotechnological tool has become increasingly vital in the removal of pollutants in water, sediments and soils because it has high impact and low cost. This happens in three major ways, namely natural attenuation, biostimulation and bioaugmentation.

In biostimulation, nutrients and minerals as well as electron acceptors and donors are added to the soil or contaminated area to enhance the biotransformation of the pollutant. Li et al. (2010) observed the effect of the iron amendment on the biodegradation of four mixed polycyclic aromatic hydrocarbons (PAHs) in mangrove sediment slurry. The highest PAH degradation was observed in the groups with iron amendment, among other factors. Shan et al. (2010) reported that the addition of lactate, corn syrup and vegetable oil sped up the transformation of trichlorofluoromethane, carbon tetrachloride and chloroform present in groundwater at an industrial site. Chen et al. (2012) also explored biostimulation with an electron donor and a shuttle for accelerating the transformation of pentachlorophenol (PCP) in iron-rich soils. When biostimulation and natural attenuation have failed or not, effective bioaugmentation is employed.

In bioaugmentation, the pollutant is removed by the addition of competent strains or a consortium of microbes (Lebeau et al. 2008). The principle behind this is that the capacity of the indigenous microbes will be enhanced by the addition of genetic diversity, leading to increased rates of biodegradation (El Fantroussi and Agathos 2005). Genetically engineered organisms designed to possess degradative capacities could also be introduced into such sites to degrade pollutants (Mrozik and Piotrowska-Seget 2010).

Natural attenuation is the reduction of contaminant population through biological, physical and chemical processes in the environment while monitoring the variation in pollutant concentration to ensure the native organisms are carrying out degradation (Kaplan and Kitts 2004; De Gisi et al. 2017). Natural attenuation is a natural tool for recycling and will happen at most polluted sites as long as the right conditions are in place. It is, however, not quick and may take a long time to complete if unaided. If this happens, bioremediation will be enhanced either by bioaugmentation or biostimulation.

## 19.5 Biodegradation Efficiency of Cassava Wastewater by Indigenous Microbes

Several technologies have been successfully used to degrade the physicochemical components of cassava wastewater. Wastewaters are mainly treated following screening, grit chamber and sedimentation, which are followed by methods utilizing activated sludge, trickling filters or lagoons to convert the non-settleable solids to settleable solids (Olaoye et al. 2018). Other methods include the use of microbial fuel cells (Olaoye et al. 2018; Izah 2019a), sedimentation, biofiltration, aerobic and sand filtration methods (Lawal et al. 2019). However, the use of biological agents is ideal for the treatment of cassava wastewater.

For instance, Lawal et al. (2019) have reported that the physicochemical characteristics of cassava wastewater such as pH, conductivity, biochemical oxygen demand, chemical oxygen demand, turbidity and hydrogen cyanide can be degraded using sedimentation (retaining cassava wastewater in treatment for 6 h), biofiltration (retaining wastewater in the chamber for 4 h) aeration (forceful aeration of the chamber for 2 h using double outlet aerator pump) and sand filtration method (using 2 mm grade fine sand in the chamber) (Lawal et al. 2019). The authors reported initial pH, conductivity, biochemical oxygen demand, chemical oxygen demand, turbidity and hydrogen cyanide of 4.6, 9.26 μS/cm, 491.7 mg/L, 485.0 mg/L, 17.30NTU and 1.3 mg/L, respectively, for after-treatment; values of 4.6, 9.60 μS/cm, 305.00 mg/L, 630.00 mg/L, 12.30NTU and 0.70 mg/L, respectively, for sedimentation method; values of 4.80, 9.70 μS/cm, 198.30 mg/L, 396.70 mg/L, 10.30NTU and 0.30 mg/L, respectively, for aerobic method; values of 5.00, 9.90 μS/cm, 136.70 mg/L, 298.30 mg/L, 10.20NTU and 0.20 mg/L, respectively, by sand filtration.

The wide use of microorganisms (especially fungi and bacteria) for the treatment of organic wastes, especially agro wastewater, has been attributed to their effectiveness in removing pathogens and accelerating the degradation process (Leow et al. 2018). The physicochemical components of cassava wastewater that can be removed by microbes include cyanide, heavy metals and other nutrients (Izah 2019b).

Cyanide is one of the major toxic substances found in cassava processing wastewater. Many microbes are able to use cyanide compounds as their sole source of energy required for growth and replication. However, some cyanide compounds are recalcitrant to degradation. Some microorganisms are very tolerant, while some bacteria that can withstand cyanide include *Microbacterium paraoxydans*, *Ochrobactrum intermedium*, *Brevibacillus brevis*, *Pseudomonas putida*, *Bacillus anthracis*, *Bacillus pumilus*, *Bacillus weihenstephanensis*, *Bacillus cereus* C1 and C2 (Kandasamy et al. 2015). Furthermore, Enerijiofi and Chukwuma (2018) reported that *Staphylococcus aureus*, *Escherichia coli*, *Aspergillus niger*, *Lactobacillus*, *Micrococcus*, *Bacillus*, *Klebsiella*, *Pseudomonas*, *Salmonella*, *Corynebacterium*, *Penicillium*, *Fusarium* and *Saccharomyces* species could degrade cyanide. Since the amount of nitrogen required for growth by these organisms is lesser than carbon requirements, it is very easy to use cyanide as the nitrogen source in the presence of another source of carbon and energy (Kandasamy et al. 2015). The authors have reported that the oxidation state of carbon (+2, like that in CO) and nitrogen (−3, like that in $NH4^+$) makes it a poor carbon source but a good nitrogen source for bacterial growth (Dursun and Aksu 2002; Kandasamy et al. 2015).

Another important constituent of cassava wastewater is its nutrient composition. These nutrients are mainly determined by the concentration of carbon, nitrogen, phosphorus and sulphur and its compounds such as nitrate, nitrite, sulphate, phosphate and carbonates. A high concentration of some of these nutrients portends adverse effects on the receiving environment, especially surface water. Excessive concentration of some of these nutrients, such as nitrates, serve as the main culprit of eutrophication. Some of these nutrients have been reported in cassava mill effluents (Izah et al. 2017b), and in surface water receiving cassava wastewater (Nwaugo et al. 2007; Omotioma et al. 2013).

Heavy metals are one of the main environmental contaminants that have been reported in several environmental matrices, including soil (Izah et al. 2017c), air (Uzoekwe et al. 2021) and water (Izah et al. 2016; Ogamba et al. 2021). Also, traces of heavy metals have been recorded in food resources (Iwegbue et al. 2013; Izah et al. 2017i). Heavy metals are recalcitrant to degradation. However, several techniques exist for their removal from wastewater. Heavy metals have been recorded in cassava wastewater contaminated soil (Nwaugo et al. 2008; Nwakaudu et al. 2012; Osakwe 2012; Igbinosa and Igiehon 2015).

Oxygen-related parameters include dissolved oxygen, chemical and biochemical oxygen demand. Dissolved oxygen is vital for life forms, specifically for organisms that utilize oxygen during aerobic respiration. The dissolved oxygen in water is influenced by many factors, including temperature and dissolved salts. Biochemical oxygen demand provides information about oxygen consumed by aerobic microorganisms during the decomposition of organic matter. Mainly, biochemical oxygen demand is influenced by nutrients in the water. Chemical oxygen demand, on the other hand, provides information about dissolved oxygen required to break down or oxidize chemical, organic materials or pollutants in water. Oxygen-related parameters have been recorded in surface waters receiving cassava processing wastewater at varying concentrations (Oghenejoboh 2015; Nwaugo et al. 2007; Omotioma et al. 2013).

The physicochemical characteristics of cassava wastewater showing their degradability by indigenous microbes is presented in Table 19.1. The study showed that conductivity, total dissolved solids, total suspended solids, salinity, hardness, biochemical and chemical oxygen demands, dissolved oxygen, sulphate, nitrate, phosphate, cyanide reduce as the biodegradation period increases. Also, nickel, iron, manganese, zinc and copper reduce, while chromium and lead concentration increase slightly as degradation proceeds. As biodegradation progresses through the use of indigenous microbes found in cassava wastewater and *Saccharomyces cerevisiae* using different methods, pH of cassava mill effluents is improved upon, thus becoming less acidic (Olaoye et al. 2018; Lawal et al. 2019; Izah et al. 2017b). Apart from indigenous microbes, other specific microbes that have been reported to play a role in the biodegradation of cassava wastewater include *Acetobacter*,

**Table 19.1** Biodegradation potentials of the physicochemical characteristics of cassava processing wastewater by microorganisms

| Parameters | Microbes | Initial value | Final value | Degradation time | Methods | Temperature | pH | Reference |
|---|---|---|---|---|---|---|---|---|
| pH | *Saccharomyces cerevisiae* | 3.93 | 6.30 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017b) |
|  | Indigenous microbes | 3.93 | 4.47 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2019a) |
|  | Microbes | 4.60 | 4.90 | – | Biofiltration | Ambient temperature | – | Lawal et al. (2019) |
|  | Indigenous microbes | 3.80 | 5.15 | – | Microbial fuel cells | – | – | Olaoye et al. (2018) |
| Conductivity, mS/cm | *Saccharomyces cerevisiae* | 14.37 | 11.07 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017b) |
|  | Indigenous microbes | 14.17 | 10.73 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2019a, b) |
|  | Microbes | 9.26 | 9.70 |  | Biofiltration | Ambient temperature | – | Lawal et al. (2019) |
|  | Indigenous microbes | 1.92 | 1.13 | – | Microbial fuel cells | – | – | Olaoye et al. (2018) |
| Total dissolved solid, g/L | *Saccharomyces cerevisiae* | 9.76 | 7.76 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017b) |
|  | Indigenous microbes | 9.71 | 7.18 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2019b) |
|  | Indigenous microbes | 1.84 | 0.98 | – | Microbial fuel cells | – | – | Olaoye et al. (2018) |
| Total suspended solid, mg/L | Indigenous microbes | 1401 | 1225.0 | – | Microbial fuel cells | – | – | Olaoye et al. (2018) |
| Hardness, mg/L | Indigenous microbes | 95.00 | 97.50 | – | Microbial fuel cells | – | – | Olaoye et al. (2018) |

(continued)

**Table 19.1** (continued)

| Parameters | Microbes | Initial value | Final value | Degradation time | Methods | Temperature | pH | Reference |
|---|---|---|---|---|---|---|---|---|
| Salinity, ppt | *Saccharomyces cerevisiae* | 7.09 | 5.57 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017b) |
|  | Indigenous microbes | 7.07 | 5.18 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2019a) |
| Temperature, °C | *Saccharomyces cerevisiae* | 27.67 | 27.20 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017b) |
|  | Indigenous microbes | 28.23 | 28.17 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2019a) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Turbidity, NTU | *Saccharomyces cerevisiae* | 854.33 | 1174.67 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017b) |
| | Indigenous microbes | 870.33 | 1304.33 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2019a) |
| | Microbes | 17.30 | 11.20 | | Biofiltration | Ambient temperature | – | Lawal et al. (2019) |
| | Indigenous microbes | 212.55 | 68.44 | – | Microbial fuel cells | – | – | Olaoye et al. (2018) |
| | *Lactobacillus* sp. | 1.48 | 8.63 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Acetobacter* sp. | 1.51 | 11.29 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Bacillus* sp. | 1.50 | 13.50 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Micrococcus* sp. | 1.41 | 9.93 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Pseudomonas* sp. | 1.50 | 19.40 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Corynebacterium* | 1.48 | 12.33 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Staphylococcus* sp. | 1.48 | 9.34 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Aspergillus* sp. | 2.77 | 12.70 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Penicillium* sp. | 4.61 | 12.43 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |

(continued)

**Table 19.1** (continued)

| Parameters | Microbes | Initial value | Final value | Degradation time | Methods | Temperature | pH | Reference |
|---|---|---|---|---|---|---|---|---|
| Dissolved oxygen, mg/L | *Saccharomyces cerevisiae* | 2.70 | 1.90 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017b) |
| | Indigenous microbes | 2.70 | 1.93 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2019a) |
| Sulphate, mg/L | *Saccharomyces cerevisiae* | 79.47 | 37.00 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017b) |
| Nitrate, mg/L | *Saccharomyces cerevisiae* | 250.00 | 80.00 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017b) |
| Phosphate, mg/L | *Saccharomyces cerevisiae* | *35.00* | 0.000 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017b) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Chemical oxygen demand, mg/L | *Saccharomyces cerevisiae* | *1663.33* | 425.00 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017b) |
| | Microbes | 485.00 | 490.00 | – | Biofiltration | Ambient temperature | – | Lawal et al. (2019) |
| | Indigenous microbes | 984.00 | 462.0 | – | Microbial fuel cells | – | – | Olaoye et al. (2018) |
| | *Pseudomonas* sp. | 106.16 | 56.06 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Bacillus* sp. | 108.49 | 58.34 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Pseudomonas* and *Bacillus* | 100.71 | 62.81 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Aspergillus* sp. | 97.85 | 48.77 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Penicillium* sp. | 110.30 | 59.15 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Aspergillus* and *Penicillium* | 108.49 | 59.70 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |

(continued)

**Table 19.1** (continued)

| Parameters | Microbes | Initial value | Final value | Degradation time | Methods | Temperature | pH | Reference |
|---|---|---|---|---|---|---|---|---|
| Biochemical oxygen demand, mg/L | Indigenous microbes | 494.88 | 173.00 | – | Microbial fuel cells | – | – | Olaoye et al. (2018) |
| | *Pseudomonas* sp. | 197.45 | 17.37 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Bacillus* sp. | 173.97 | 19.82 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Pseudomonas* and *Bacillus* | 170.45 | 4.39 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Aspergillus* sp. | 99.65 | 28.71 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Penicillium* sp. | 91.18 | 28.23 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| | *Aspergillus* and *Penicillium* sp. | 87.90 | 21.69 | 8 | Shake flask degradation method | Ambient temperature | – | Enerijiofi et al. (2017) |
| Lead, mg/L | Indigenous microbes | 0.05 | 0.08 | – | Microbial fuel cells | – | – | Olaoye et al. (2018) |
| Copper, mg/L | *Saccharomyces cerevisiae* | 1.46 | 0.81 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017a) |
| Zinc, mg/L | *Saccharomyces cerevisiae* | 4.35 | 3.21 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017a) |
| Manganese, mg/L | *Saccharomyces cerevisiae* | 4.64 | 2.25 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017a) |
| Iron, mg/L | *Saccharomyces cerevisiae* | 28.27 | 13.34 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017a) |
| | Indigenous microbes | 0.03 | 1.00 | – | Microbial fuel cells | – | – | Olaoye et al. (2018) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Chromium, mg/L | *Saccharomyces cerevisiae* | 0.18 | 0.29[a] | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017a) |
| Nickel, mg/L | *Saccharomyces cerevisiae* | 1.81 | 0.63 | 15 | Aerobic fermentation | Ambient temperature | Not controlled | Izah et al. (2017a) |
| Magnesium, mg/L | Indigenous microbes | 217.50 | 210.50 | – | Microbial fuel cells | – | – | Olaoye et al. (2018) |
| Hydrogen cyanide, mg/L | Microbes | 1.30 | 0.40 | | Biofiltration | Ambient temperature | – | Lawal et al. (2019) |
| Cyanide, mg/L | Indigenous microbes | 33.00 | 32.00 | – | Microbial fuel cells | – | – | Olaoye et al. (2018) |

[a] Values showed an apparent increase which did not differ significantly

*Bacillus*, *Micrococcus*, *Lactobacillus*, *Corynebacterium*, *Pseudomonas*, *Staphylococcus*, *Aspergillus* and *Penicillium* species and *Saccharomyces cerevisiae* (Table 19.1).

## 19.6 Factors that Influence the Biodegradation of Cassava Wastewater by Microorganisms

### *19.6.1 Presence of Inhibitory Materials*

The presence of inhibitory materials play an essential role in the ability of microorganisms to degrade wastewater from organic sources. For instance, Enerijiofi and Chukwuma (2018) reported that cassava wastewater supplemented with 30 ppm of cyanide, with inoculum size of 1.5 x10(Asogwa et al. 2015) CFU/ml and pH of 6 for 8 days, with concentration of inhibitory materials (phenol) of 0.30%, 0.50%, 0.70%, 0.90% and 1.10% for 8 days had the degradation rates of 40.90%, 45.63%, 48.20%, 47.93% and 49.33%, respectively, for Bacillus sp., 40.13%, 45.60%, 49.13%, 47.27% and 48.10%, respectively, for Pseudomonas sp. and 44.80%, 48.20%, 48.43%, 49.77% and 49.17%, respectively, for *Aspergillus niger*. As the quantity of inhibitory materials increases, the ability of test organisms to degrade toxicants such as heavy metals and cyanide is affected. For instance, some toxic metals such as copper, chromium, cobalt, vanadium can hinder the activities of microbes during the removal of heavy metals. This is because these metals possess the tendency to hinder the activity and metabolism of microorganisms due to their toxicity.

### *19.6.2 Inoculum Size*

The size of the inoculum plays an essential role in the degradation of organic substrates. This is because when the population of viable organisms is inadequate, it may influence the tendency of organisms to metabolize some of the toxic substances found in cassava wastewater. Enerijiofi and Chukwuma (2018) reported that medium with pH of 6.0 and 30 ppm of cyanide at inoculum size of 2 mL, 3 mL, 4 mL, 5 mL and 6 mL for 8 days had degradation rate of 38.10%, 40.70%, 39.97%, 32.37% and 30.27%, respectively, for Bacillus sp., 38.13%, 32.57%, 30.90%, 31.27% and 28.97%, respectively, for Pseudomonas sp. and 51.03%, 43.53%, 42.50%, 37.50% and 39.50%, respectively, for *Aspergillus niger*. The results showed that the larger the inoculum size at pH of 6 for 8 day period, the higher the degradation rate.

### 19.6.3 The Concentration of Toxic Substances

The concentration of toxicants such as cyanide influences the biodegradation potential of cassava mill effluents. Enerijiofi and Chukwuma (2018) reported that medium with inoculum size of 1.5 × 10(Asogwa et al. 2015)CFU/ml at pH of 6 for 8 days when the cyanide content was 30, 60, 90, 120 and 150 ppm had degradation rates of 75.33%, 92.62%, 96.06%, 83.07% and 84.71%, respectively, for Bacillus species, 67.27%, 82.38%, 89.31%, 94.12% and 97.00%, respectively, for Pseudomonas species and 82.00%, 93.38%, 91.22%, 84.85% and 92.23%, respectively, for *Aspergillus niger*. This indicates that the concentration of cyanide plays an essential role in its degradation from the environment. It also suggests that when the concentration of cyanide is very high, organisms may become stressed, thereby leading to the alteration of some of its metabolic processes, which tends to alter its potential to remediate cyanide from the environment.

### 19.6.4 pH

pH is one of the parameters that influence several environmental activities. pH plays an essential role in determining the activities of living organisms, especially microorganisms. This is because microorganisms have the tendency to survive in varying pH conditions. For instance, archaea organisms such as *Picrophilus oshimae,* an acidophile can thrive in pH of 0.1–4.0, *Natronobacterium gregoryi*, an alkaliphile, can thrive in pH of 8.0–12.0. Others require varying pH conditions for growth, including *Salmonella* species (6.0–12.0), *E. coli* (5.5–12.0), *Campylobacter* species (6.0–11.5), *Vibrio* species (6.0–11.5), *Staphylococcus* (6.0–13.0), lactic acid bacteria (3.0–14.0), yeast (2.0–12.0) and moulds (1.00–14.00). Enerijiofi and Chukwuma (2018) reported percentage degradation of cassava wastewater medium with inoculum size of 1.5 x10(Asogwa et al. 2015)CFU/ml and cyanide content of 30 ppm for 8 days at pH of 4.0, 5.0, 6.0, 7.0 and 8.0 as 34.87%, 32.13%, 27.63%, 40.07% and 47.97%, respectively, for Bacillus sp., 44.50%, 34.73%, 25.50%, 38.57% and 48.20%, respectively, for Pseudomonas species and 45.17%, 41.13%, 38.17%, 46.27% and 49.10%, respectively, for *Aspergillus niger*. The study also showed that pH of 6 is best for the degradation of cyanide using the test organisms and the same inoculum size.

### 19.6.5 Incubation Period

The incubation period of an organism plays an essential role in its growth and function. Different organisms have varying degradation periods. Agarry and Owabor (2012) reported the degradation of cassava mill effluents with different organisms such as *Bacillus pumilus*, *Bacillus megaterium*, *Bacillus subtilis*, *Flavobacterium rigensis*, *Klebsiella pneumoniae* and *Pseudomonas putida.* The authors also reported that *Pseudomonas putida* degrades cyanide more at <100 h as compared to other test organisms.

### 19.6.6 Choice of Microorganisms

Due to changes in the biochemical composition of different test organisms, their ability to degrade toxicants varies. Also, the physical composition of toxicants, oxygen and nutrients requirements, temperature, salt and pH tolerance ability of the organisms also influence their ability to degrade toxicants. In cassava wastewater, studies have shown that different organisms portend varying effects in the degradation of cyanide (Agarry and Owabor 2012; Enerijiofi and Chukwuma 2018). For instance, Agarry and Owabor (2012) reported that *Bacillus pumilus*, *Flavobacterium rigensis*, *Bacillus subtilis*, *Bacillus megaterium*, *Pseudomonas putida* and *Klebsiella pneumoniae* have the ability to degrade cyanide by 78%, 82%, 88%, 60%, 94% and 68%, respectively.

### 19.6.7 Nutrients

Some bacteria that can utilize cyanide as the sole source of carbon are also found in cassava mill contaminated environment. Some of these organisms include *Bacillus pumilus*, *Bacillus cereus* and *Pseudomonas putida* (Kandasamy et al. 2015). When a medium containing cyanide and glucose was increased to 5 mM, cyanide removal rate increased up to 63% (*Bacillus* pumilus) and 61% (*Pseudomonas putida*). This suggests that nutrients such as glucose are critical for the removal of toxicants such as cyanide (Kandasamy et al. 2015).

### 19.6.8 Hydraulic Retention Time and Organic Loading Rate

Hydraulic retention time (HRT) is one of the indicators commonly used to determine the efficiency of the wastewater treatment chamber or configuration, while the organic loading rate (OLT) is the number of organic materials that are treated in a given volume of wastewater in a treatment configurator at a given time interval. According to Ohimain and Izah (2017), OLR has a relationship with the HRT during wastewater treatment. The microbial community and population play an essential role in determining both HRT and OLR during the treatment of wastewater. At short HRT, the OLR is high over at configurator with stable organic constituents and another ideal intrinsic and environmental factors. In Cassava wastewater, Lawal et al. (2019) reported that degradation of wastewater microbes reduces the organic load. The authors further noted that longer hydraulic retention time leads to higher biodegradation of organic substrates.

## 19.7 Conclusion

Cassava is a primary staple food that is processed into gari, fufu, flour, etc. The production of gari from cassava tubers accounts for over 60% of its economic importance in the largest producing nations. In Nigeria, the largest cassava producing country, rudimentary equipment is prevalently used for food processing. Also, effluents generated from the mills are rarely treated before environmental discharge. As such, the effluents resultantly impact the receiving environment and associated biota. Due to the ubiquitous nature of microbes, they invade effluents and degrade the physicochemical properties, especially its acidity (pH), oxygen-related parameters such as biochemical and chemical oxygen demands, nutrients (nitrate, phosphate, sulphate, etc.). The genera of microorganisms which include fungi (moulds and yeasts) and bacteria that often degrade cassava processing wastewater include *Acetobacter*, *Bacillus*, *Micrococcus*, *Lactobacillus*, *Corynebacterium*, *Pseudomonas*, *Staphylococcus*, *Aspergillus* and *Penicillium* and *Saccharomyces*. Meanwhile, the efficiency of these microbes is affected by factors such as temperature, pH, nutrients, oxygen, photo-oxidation, bioavailability and presence of inhibitory materials, among others.

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