Rangabhashiyam Selvasembian
Eric D. van Hullebusch
Joyabrata Mal *Editors*

Biotechnology for Environmental Protection

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Rangabhashiyam Selvasembian works as Assistant Professor in the School of Chemical & Biotechnology, SASTRA Deemed University, India. He received his Doctor of Philosophy degree from National Institute of Technology Calicut, India. He has received Post-Doctoral Fellowship from Max Planck Institute for Dynamics of Complex Technical Systems, Germany, received National Post-Doctoral Fellowship from SERB-DST, India, selected as Young Scientist by DST, India, for the BRICS Conclave held in Durban, South Africa, and received Hiyoshi Young Leaf Award from Hiyoshi Ecological Services, Hiyoshi Corporation, Japan. His major research interests are bioremediation and wastewater treatment. He is an editor and editorial board member of various international journals. He has published over 95 articles and also contributed several book chapters in addition to editing books.

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Environmental Pollutants: Metal(loid)s and Radionuclides

1

Wisdom A. Munzeiwa, Deborah T. Ruziwa, and Nhamo Chaukura

Abstract

Anthropic inputs of toxic metals into the environment pose a serious environmental and human health risk globally. Whereas some metals such as copper, manganese, nickel, and zinc are essential in regulating biological processes in living organisms, many metal(loid)s such as arsenic, cadmium, chromium, mercury, and germanium are toxic even at low concentrations. Moreover, some metals and metal(loid)s such as uranium, strontium, and cesium have radioactive properties and, as such, are classified as radionuclides. Metal(loid)s and radionuclides are nonbiodegradable persistent pollutants which originate from agricultural, domestic, and industrial effluents; hence, they pose a threat to the environment. Since humans constitute the highest trophic level, and toxic metals are biomagnified along the food chain, humans have a higher likelihood of suffering serious health problems. For instance, metal(loid)s and radionuclides can potentially cause cancer, damage of vital organs, nausea, and vomiting. A number of chemical and physical removal methods have been explored, but their limitations, such as the generation of secondary pollution, the intricate subsequent processing, and the high cost, make them inefficient. In view of this, microbial bioremediation, specifically the application of bacteria, has attracted attention owing to the feasibility and efficiency of the technique in removing toxic metals from aquatic systems. Bacteria remove metal(loid)s and radionuclides through

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adsorption, biosorption, efflux, and general resistance mechanisms. This chapter discusses various sources of toxic metal(loid)s and radionuclides, their occurrence, and bioremediation of contaminated aquatic systems.

Keywords

Bacteria · Biopolymers · Bioremediation · Radioisotopes · Toxicity · Wastewater

1.1 Introduction

Some metal(loids) and radioisotopes or radionuclides exist in the natural foundation of the earth's crust. Metal(loid)s and radionuclides have attracted great attention from policy makers, the public, and academia due to potential harmful effects to humans and the ecosystem (Ugbede et al. 2020). Recent technological advances in medicine, information technology, energy, and ammunitions have resulted in an increased element extraction and their subsequent transfer to the environment (Gwenzi 2020). The increased amounts overload the ecosystem's natural cycles and, hence, become harmful when taken up by the living organisms. Consequently, extensive amounts of these element's pollutants are witnessed on a global scale, and their effects are far-reaching (Yanguo et al. 2003). The occurrence behaviour, and detrimental effects of these contaminants are witnessed in geological formations, soils, plants, and aqueous systems and the atmospheric space. The radionuclides and metal(loids) tend to bioaccumulate and biomagnify in the ecological food chain; hence, they pose environmental and health risks (Table 1.1) (Tchounwou et al. 2012).

Water is one of the most essential natural resources, and it supports humans, animals, plants, and other living organisms in the ecosystem (Liu et al. 2021a, b). Metal(loid)s and radionuclides co-exist in both biotic and abiotic systems of aquatic environments at varying concentrations. Aquatic environments often act as a sink for metalloids and radionuclides (Fig. 1.1), which usually adsorb on solid sediment matrices and are resuspended via bioturbation and hydraulic drift (van de Velde and Meysman 2016). Nevertheless, toxicity in aquatic organisms transpires when uptake supersedes rates of efflux and detoxification of metal into metabolically passive forms (Perera et al. 2016). The nonbiodegradability, persistence, and toxicity of these metal ions are a threat to environmental and human health. Toxic metals give rise to various complex human health challenges including damage of cellular components, cancer, impairment of brain and lung function, and nausea (Ghimire and McCarthy 2018).

The main mode of transport of radionuclides and metal(loid)s is via atmosphere, oceanic currents, and rivers (Lokas et al. 2017). The atmosphere provides an easy passage of pollutants, for example, plutonium and nonnatural uranium were detected in a radius of 120 km from the Fukushima few days after explosion (Shinonaga et al. 2014). This aerial transport mechanism presents a potential health risk not only to the immediate environment. For example, elevated radionuclides and metal(loid)s have

Table 1.1 The anthropic sources and permissible limits of metal(loid)s in the environment and their human health effects

Metal (loid)	Anthropogenic source	Permissible limits in drinking water (source USEPA) and soil (source EU)	Toxic effects
Lead	Mining, plumbing, leaded gasoline, lead-acid batteries	0.05 mg/L in drinking water, 300 mg/kg in soil	Can cause serious injury to the brain, nervous system, red blood cells, and kidneys, anorexia, and weakness of joints
Chromium	Metal(loid) plating, industrial and domestic waste, mining and mineral leaching	0.05 mg/L in drinking water, 150 mg/kg in soil	Allergic dermatitis in humans, causes liver and kidney damage, internal hemorrhaging, and respiratory damage
Arsenic	Natural processes, industrial activities, pesticides, industrial waste, smelting of copper, lead, and zinc	0.05 mg/L in drinking water	Skin damage and increased risk of cancer and problems with the circulatory system
Mercury	Industrial waste; mining; pesticides; coal; electrical equipment, e.g., batteries, lamps, and switches; smelting; and fossil fuel combustion	0.002 mg/L in drinking water	Is associated with kidney damage and nervous system disorders
Zinc	Industrial waste, metal/ metalloid plating, plumbing	5 mg/L in drinking water, 300 mg/kg in soil	Inhibits the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter
Cadmium	Industrial discharge, mining waste, metal/ metalloid plating, water pipes, batteries, paints and pigments, plastic stabilizers, and landfill leachate	0.005 mg/L in drinking water, 3 mg/kg in soil	Kidney dysfunction if there is chronic accumulation in the kidneys, causes high blood pressure, destroys testicular tissue and red blood cells

been reported in Asian and European glaciers (Baccolo et al. 2017) and in remote Arctic and Antarctic areas (Singh et al. 2013). Ultimately, soils and water bodies are the major sink for metal(loid)s and radionuclides released into the environment, and most of these toxicants do not undergo microbial or chemical degradation (Kirpichtchikova et al. 2006).

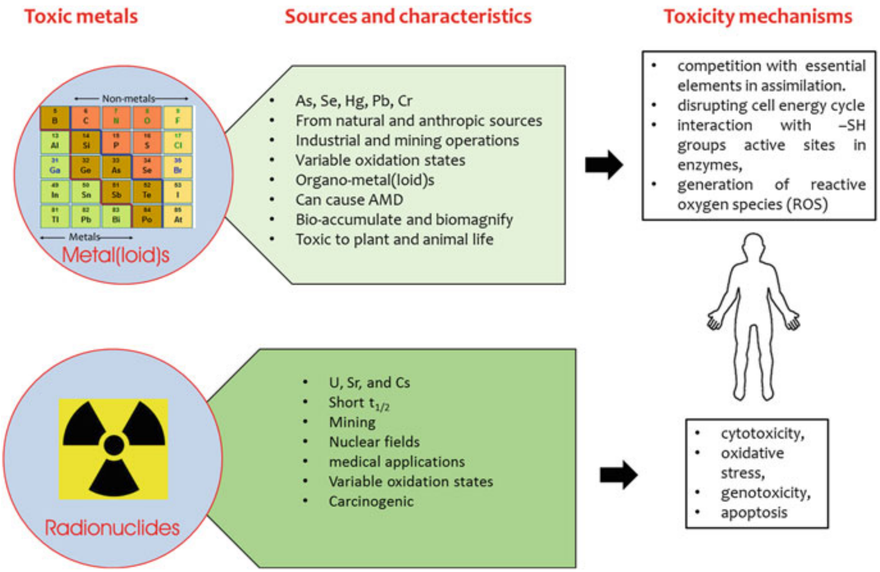

Fig. 1.1 Sources, characteristics, and toxicity mechanisms of metal(loid)s and radionuclides

1.1.1 Mining and Environmental Impact

The occurrence of toxic metals adversely affects the atmosphere, biosphere, hydrosphere, and lithosphere (Jain 2015). Soils are the major sinks for heavy metals released into the environment by most anthropogenic activities. Generally, heavy metals are recalcitrant to chemical or microbial degradation, and consequently, they persist after being emitted into the environment. The accumulation of metals in agricultural soils has resulted in severe ecological impacts (Wuana and Okieimen 2011). The occurrence of acid mine drainage is another environmental hurdle that is associated with mining (Research Watch: Acid mine drainage 1997). Usually, acid mine drainage (AMD) originates from uncovered rocks containing sulfide compounds, which are oxidized into sulfuric acid upon exposure to air. The chief contributor is pyrite (FeS_2) which releases high concentrations of iron responsible for red-colored iron hydroxides. The problem is further worsened by the acidic water which further dissolved the rocks mobilizing the metalloids and nuclides into the environments (Karpinsky et al. 2020). AMD can destroy the biological activity and water quality of ground and surface water rendering them unusable.

1.2 The Occurrence of Selected Metal(loid)s

1.2.1 Cadmium, Chromium, Arsenic, Lead, and Mercury

Cadmium is abundant in the earth's crust, and it is translocated to the surface via land excavation, mining, weathering of cadmium-rich rocks such as greenockite, and volcanic activities (Suhani et al. 2021). Anthropogenic cadmium emissions are mainly through activities such as mining and smelting, waste disposal, and agricultural inputs and waste (Zhang et al. 2020). Cadmium is also used as a corrosion inhibitor in metallic objects, pigment in glass industry, stabilizer for polyvinyl chloride (PVC), and electrodes in Cd/Ni batteries and semiconducting solar panels. Hence, recycling and incineration of these Cd materials also contribute to the high levels in the environment. In aquatic systems, the divalent Cd(II) is most prevalent, and it is immobilized as sulfide or oxides in rock sediments.

Chromium mainly exists as chromite spinel ($FeCr_2O_4$) and is found in industrial activities such as electroplating, ore refining, paper making, steel smelting, tanning, and automobile manufacturing (Kim et al. 2015). Chromium commonly exists in two main oxidation states contingent on the pH and redox conditions. Cr(VI) is the prevailing species under aerobic conditions, and under anaerobic surroundings, it can undergo reduction to Cr(III) in the presence of soil organic matter, inorganic sulfide (S^{2-}), and ferrous (Fe^{2+}) ions (Simon 2014). Cr(III) is an essential trace element and is nontoxic to small aquatic animals at very low concentrations. Moreover, it has limited mobility and bioavailability owing to the poor solubility of $Cr(OH)_3$ under neutral pH conditions (DalCorso 2012). In contrast, Cr(VI) occurs as highly soluble and, thus, mobile oxyanionic $CrO_4{}^{2-}$ and $Cr_2O_7{}^{2-}$ species (Xiao et al. 2013). Consequently, these species easily adsorb onto soil particles, particularly iron and aluminum oxides, and are, thus, carcinogenic.

Naturally, arsenic predominantly exists as tennantite ($Cu_{12}As_4S_{13}$) and enargite ($CuAsS_4$) in copper ores. Leaching and corrosion of arsenic-containing minerals, rocks, and soils release As into the environment (Long et al. 2012). Mining contributes greater anthropogenic proportion of As in the environment. Due to the resemblance in physicochemical properties of Cu-S and Cu-As-S, it is problematic to conventionally separate them during copper extraction; consequently, As is found in the smelting waste (Zhou et al. 2021). Other anthropogenic sources include agricultural chemicals and waste, feed additive, landfill leachates, alloying industries, and coal combustion (Yadav et al. 2021). The chemistry of As is fairly complex, and it exists in four major oxidation states (−3, 0, +3, +5). Under an aerobic environment, As(V) is prevalent, usually as arsenate ($AsO_4{}^{3-}$) (pH 7–11) in various protonation states depending on the pH: $HAsO_4{}^{2-}$ (pH 7–11), $H_2AsO_4{}^{-}$ (pH 3–6), and H_3AsO_4 (pH 0–2) (Flora 2015). Under reducing conditions, As(III) is the dominant species, existing as $AsO_3{}^{3-}$ (pH 14) and its protonated forms, namely, H_3AsO_3 (pH 0–9), $H_2AsO_3{}^{-}$ (pH 10–12), and $HAsO_3{}^{2-}$ (pH 14). The inorganic arsenates can be biotransformed by different enzymes or microbes to methyl and aromatic organoarsenical compounds (Acquavita et al. 2021). The most common organoarsenic species are methylated forms of arsenite ($RAsH_2$, R_2AsH, and

R_2As, where R = alkyl or aryl) and arsenate ($RAsO_3H_2$, $R_2AsO_2H_2$, R_3AsO, R_4AsO^+). These derivatives are highly volatile and can be easily discharged into the atmosphere (Hussain et al. 2021).

Lead exists naturally in the soil from biogeochemical processes such as weathering of granitic rocks (Lovering 1969). Common anthropic sources of Pb in the environment include agrochemicals; automobile exhausts; burning of coal; effluents from battery, mining, plating, and leather tanning industries; ore smelting; finishing processes; and additives in paints (Kushwaha et al. 2018). Lead has been used in the manufacture of munitions for many centuries, and this has resulted in high Pb concentrations in shooting ranges (Dinake et al. 2019). Lead(II) is the most prevalent inorganic and reactive species, forming mono- and polynuclear species with anions such as PO_4^{2-}, OH^-, Cl^-, and CO_3^{2-}. The general Pb species that are emitted into groundwater, surface water, and soil are ionic Pb, Pb(II), Pb oxides and hydroxides, and lead-metal oxyanion complexes. Pb may be complexed to organic ligands such as amino acids, humic acids, and fulvic acids to form organometallic complexes. It is also found adsorbed on biological material, Fe/Mn oxides, organic matter, and clay colloidal particle surfaces (Manceau et al. 1996). The mobility and bioavailability of Pb species in soils and sediments largely depend on the partitioning of water-soluble and exchangeable; organic-, anion-, and oxide-bound; and residual fractions. Apart from the inorganic Pb compounds, there are a number of organolead compounds. Tetraethyllead (TEL) and tetramethyllead (TML) are the most common which are introduced anthropically through gasoline combustion and exhaust emission (Gallert and Winter 2002). Under anaerobic environments, the inorganic lead can be transformed to organolead due to microbial alkylation. The alkylated species are readily bioaccumulated, but the more volatile methylated forms are less toxic than the ethylated species. Through photo- or UV irradiation and hydroxyl radicals, atmospheric TEL and TML are degraded to the more stable and water-soluble ionic tri- and di-alkylated forms ($R_3Pb^+ > R_2Pb^{2+}$, $R = –CH_3$ or $–C_2H_5$) (Pyrzyńska 1996).

Mercury like any other metal(loid)s is introduced into the atmosphere from natural and anthropic sources. Anthropic sources of Hg are combustion of fuels, medical and municipal sewage waste, high-temperature metal extraction processes, fluorescent lamps, and mine tailing. Natural sources include volcanoes, hydrothermal activity, and biomass burning (Rodriguez Martin et al. 2021). Hg a liquid at room temperature behaves unique compared to other metalloids due to the formation of more volatile alkylated species. Mercury speciation also depends on the environmental conditions, and it mainly exists as elemental (Hg^0), divalent inorganic (Hg (II)), and organomercury (monomethylmercury (MMHg), dimethylmercury (DMHg)) (Zhang et al. 2014). Atmospheric Hg pollutant species can be designated as gaseous elemental Hg (GEM or Hg^0), gaseous oxidized Hg (GOM), and particulate-bound Hg (PBM) (Landis et al. 2002). The atmospheric space is the more probable gateway conduit for the speedy and long-range delivery of Hg. The species present in the atmosphere are wet/dry deposited on the terrestrial system (Álvarez-Fernández et al. 2020). The bulk of mercury in terrestrial systems accumulates in soil and interacts with organic matter, and some are assimilated by the plants, and a certain fraction is recycled back into the atmosphere. In aquatic systems, microbes transform inorganic mercury (Hg(II)) to methylated Hg as time progresses. Mercury (Hg) is an element that has posed a greater health risk because it is non-essential to biological functions in different species (Panagos et al. 2021). The methylated species pose a greater health risk because they can bioaccumulate, and the effects are further amplified via biomagnification in the food chain. The mercury organic species are reported to be highly neurotoxic, and in humans, the main source of intake is via the consumption of fish species (Selin 2009).

Industrial and mining operations account for about 40% of selenium present in the atmospheric and aquatic systems (Gebreeyessus and Zewge 2018). Selenium is an essential trace metal in metabolic processes in living organisms. Notwithstanding, due to bioaccumulation potential and terrestrial immobilization, it is a potential toxin (Trippe and Pilon-Smits 2021). The speciation of Se in different environments depends on the biological, physical, and chemical factors, which influence their oxidation state and transformation. Selenium mainly exist as inorganic and organometallic species in different matrixes and environments (Sinharoy and Lens 2020). The inorganic Se species are mainly prevalent in aquatic systems as found in selenide (Se^{2-}), oxyanions (selenite, SeO_3^{2-}, and selenate (SeO_4^{2-})), and insoluble elemental selenium (Se^0) (Fernández-Martínez and Charlet 2009). Microbial organism can transform the inorganic Se species to organic selenium species which are more predominant in the air, soil, and plants, mainly alkylselenides (methyl selenides, SeMet), trimethylselenonium ($Se(Met)_3$), and selenoamino acids (e.g., selenocysteine (SeCys)) (Abu-Erreish et al. 1968; Tan et al. 2016). The mobility, behavior, and fate of Se in soil are species dependent and are controlled by biogeochemical cycle processes such as biomethylation, oxidation-reduction, sorption, precipitation, and complexation (Jurinak and Tanji 1993). In the soil, the main contributing factors are pH, redox conditions, soil type, mineral content, organic matter, microbial activity, and competing ions. In soil and sediments, selenate is more soluble and bioavailable compared to selenite and S^0, which are strongly adsorbed (Gedik et al. 2016).

1.2.1.1 Effect of Metal(loid)s on Environmental and Human Health

Environmental pollutant exposure has contributed to the greater number of diseases, which have led to premature deaths worldwide. Though environmental pollution is a global misery, its overwhelming effects are unevenly distributed to low-income and/or marginalized communities (Fernández-Llamazares et al. 2020).

Metal(loid)s generally induce toxicity effects, and the toxicological mechanisms are almost similar in both plant and animal life. However, the effects, signs, and symptoms are expressed differently. Plants tend to respond to higher metalloid lethal doses because they have a counterbalance response mechanism to reduce the negative effects. Some plant species (hyperaccumulators) can even accumulate over 100 g/kg dry weight (Singh et al. 2016). Metalloids exert their bio-toxicity in four mechanisms:

1. Similarities in physiochemical properties to some essential elements, and as a consequence, there is competition in assimilation. As(V) in arsenate (AsO_4^{3-}) parallel P in phosphate (PO_4^{3-}) disrupting cell energy cycle.
2. Interaction of metalloids with sulfhydryl group (-SH) active sites in enzymes, which interrupts their function and conformational structure.
3. Dislodgment of co-factor cations causing malfunctions.
4. Generation of reactive oxygen species (ROS), which subsequently destroy the macromolecules (Oehme 1972; Hossain et al. 2012).

The microbiota are not spared by the mining effects which has a potential to reduce microbial biomass and biodiversity. A previous study demonstrated that the accumulation of metalloids in soil above a certain threshold value inhibited the microbial growth and activity and extended the flowering period of crops (Nayak et al. 2015). The excess of essential and nonessential metal(loids) usually induces toxicity effects on plants, such as chlorosis, reduced biomass buildup, inhibition of photosynthesis and growth, water imbalance and impaired nutrient assimilation, and senescence (Yadav 2010; Singh et al. 2016). Numerous investigations have reported phytotoxicity, food chain contamination, and human health effect from various geographical locations (Romero-Estevez et al. 2020; Briffa et al. 2020; Liu et al. 2021a, b; Chirinos-Peinado and Castro-Bedrinana 2020; Wang et al. 2020). A greenhouse experiment demonstrated Pb induces oxidative stress in plants via ROS generation and caused plant cell death (Sidhu et al. 2016). Another study described arsenic metal contamination of vegetables farmed on mine drainage-polluted soil and the associated human health risk (Qin et al. 2021). A study assessed the levels of seven metal(loid)s (As, Cd, Cr, Cu, Ni, Pb, and Zn) in cereals and pulses and linked health inferences in Bangladesh (Islam et al. 2014). Of concern was the higher carcinogenic risk of arsenic (5.8×10^{-3}) and lead (4.9×10^{-5}) which surpassed the US Environmental Protection Agency accepted risk level of 1×10^{-6}.

Several studies also document the adverse effects of metalloids in aquatic organisms (Bosch et al. 2017). Aquatic organisms can bioaccumulate metalloids directly from surrounding waters and sediments or through ingestion via the food chain. A previous study investigated toxic metals (Pb, Hg, Cu, Cr, Cd, and As) in crabs, fish, and shrimp and observed that the metalloid concentrations varied from one species to another depending on season and location (Yu et al. 2020). For example, high concentrations were observed in autumn and summer and decreased in spring and winter. Also, Cd levels were much higher in crab posing a greater risk of toxicity to other organisms along the food web. Metal(loid) toxicity is not limited to humans through food chain contamination, but livestock health is also at risk. Previous studies have detected excess metalloids in the animal edible portion's body tissues and fluids (milk) as well as blood and eggs (Boudebbouz et al. 2021). A related study reported duck meat metalloids' concentrations which were higher than the recommended values for $Pb = 5429$ mg/kg, $Cd = 1.348 \times 10^{-3}$ mg/kg, $Co = 1.229 \times 10^{-3}$ mg/kg, and $Cr = 1.45 \times 10^{-3}$ mg/kg (Aendo et al. 2019). Investigations of metalloids' (Cd, Cu, Fe, Hg, Mn, Pb, and Zn) concentrations in meet and meet products by Alturiqi and Albedair (2012) showed that the recoverable concentrations ranged between 0.125 and 242.44 μg/g and were above the Joint FAO/WHO and EC Committees recommendations.

1.2.2 Radioactive Pollutants

Radioactive pollution is evident through the sudden rise in the natural background radiation levels in the environment. This is caused by uncontrolled activities in different nuclear fields and is characterized by the emission of radioactive pollutants into the ecosystem. A number of radionuclides are responsible for this pollution, and these commonly include uranium, strontium, and cesium.

1.2.2.1 Uranium, Strontium-90, and Cesium-120

Uranium (U) is a ubiquitous element with 14 radioactive isotopes. In the natural environment, U occurs as a mixture of ^{238}U, ^{235}U, and ^{234}U. Of these, ^{235}U is fissionable, while ^{238}U is the most abundant (99%) and ^{234}U the least abundant (0.0057%). Nuclear fission decays ^{234}U ($t_{1/2} = 2.5 \times 10^5$ years) to a string of radionuclides to generate the stable ^{206}Pb, alongside emission of α- and β-particles and γ-rays. ^{235}U ($t_{1/2} = 7 \times 10^8$ years) and ^{238}U ($t_{1/2} = 4.5 \times 10^9$ years) decay to stable ^{207}Pb and ^{206}Pb nuclides, respectively, also emitting α- and β-particles and γ-rays. Of notable concern, during the fission process of natural uranium decay chain, radioactive radon gas ^{222}Rn ($t_{1/2} = 3.8$ days) nuclide is produced, and because it is more volatile, it can easily escape into the atmosphere. Uranium presents variable oxidation states (+2, +3, +4, +5, and +6), although the quad- and hexavalent form are more prevalent. In nature, uranyl oxygen species are more common although they can also complex with other anions, e.g., phosphates and carbonates. In abiotic processes, U^{4+} occurs in strongly reducing locations, and its formation is coupled to the oxidation of soil organic matter or iron. When complexed by inorganic ligands such as F^-, Cl^-, $SO_4{}^{2-}$, and $PO_4{}^{2-}$, U^{4+} is usually insoluble and immobilized in the soil. The U^{6+} occurs in oxidizing surroundings and is more soluble and mobile. In the abiotic processes, geochemical recycling of uranium is also coupled to biogenic transformation. Under certain conditions, uranium redox processes are mediated by microbial organisms. Bio-assimilation in aquatic organisms is due to cationic or neutral aqueous U complexes, i.e., $UO_2{}^{2+}$, $UO_2(OH)^+$, $UO_2(OH)_2$, and UO_2CO_3, whereas Muller (2002) proposes the integration of phosphate species (Markich 2002; Beaugelin-Seiller et al. 2009). Other studies have also shown that phosphate species (Muller 2002), bicarbonate, and carbonate anions $(UO_2CO_3)_2{}^{2-}$ (Croteau et al. 2016) can also be translocated across cell membranes.

Strontium has four naturally occurring isotopes (^{84}Sr, 0.56%; ^{86}Sr, 9.87%; ^{87}Sr, 7.04%; and ^{88}Sr, 82.53%). All these isotopes are stable, although the proportion of ^{87}Sr differs due to the radioactive decay of ^{87}Rb. Strontium-90 (^{90}Sr) is a radioactive isotope of strontium (Sr) which is toxic with a $t_{1/2}$ of 29 years, which is only produced by nuclear fuel irradiation. Analysis of ^{90}Sr (β-emitter, $\beta_{\max}$ 546 keV) with a liquid scintillation counter or gas proportional counter in environmental matrixes is a bit challenging, because of interference from other β-emitters (Torres et al. 2000). ^{90}Sr is one of the important fission byproducts of uranium and plutonium likely to be found in the environment around nuclear power plants or fuel reprocessing plants. Similar to its group II counterpart calcium (Ca), ^{90}Sr is very mobile and extensively dispersed in groundwater located near nuclear reactor plants and waste management areas. As a result, it can be accumulated in bones, resulting in bone cancer and leukemia. Strontium-90 is a pure β-emitter, like its nuclear chain decay daughter product ^{90}Y ($t_{1/2} = 64.2$ h). ^{90}Sr is a non-redox active radionuclide present primarily as the Sr^{2+} ion. ^{90}Sr present in sediments is linked to the divalent $^{90}Sr^{2+}$ions and at neutral pH usually forms outersphere complexes that electrostatically adsorb on clay and metal oxide mineral surfaces.

Cesium (Cs) is a group I alkali metal with chemical properties analogous to those of K, which is a macronutrient element of plants. The toxicity of Cs to living organisms is not due to the stable isotope (^{133}Cs), but from the artificially produced radioactive ^{134}Cs and ^{137}Cs. The most stable radio cesium isotopes are ^{134}Cs and ^{137}Cs (with $t_{1/2}$ of 2.07 years and 30.1 years, respectively). Other radioisotopes are short-lived with half-life of few seconds (e.g., ^{120}Cs, $t_{1/2} = 61.2$ s).

1.2.2.2 Sources and Transport of Radioactive Pollutants

The nuclear fuel cycle requires mining and milling of uranium-laden ores as the primary step, producing residual wastes which end up in the environment. Three mining methods are employed, namely, surface, underground, and solution mining, depending on factors such as ore grade, size, location, geology, and economic feasibility. Open-pit mining generates considerable amounts of radioactive barren rock and overburden waste. Land disturbance from modern mineral extraction is likely to increase the concentrations of dissolved and suspended non-radioactive substances in surface water. Increased storm water runoff due to mining is mostly ascribed to a reduction in interception storage by vegetation and soil infiltration capacity since vegetation and soils are removed before mining operations. Leaching involves the use of alkaline or acid solution to dissolve the uranium, and the water is pumped out for recovery. In the process, uranium in conjunction with other heavy metals, are mobilized pollute aquifer and surface water making it unsuitable for farming or human consumption. Solid wastes at uranium mill tailing sites comprise of leached ore residues and solids produced from waste treatment processes which include sludge. Uranium mill tailings mainly harbor the radioactive element radium (Abdelouas 2006). Overflow from the mine waste stockpiles and aqueous waste from the milling process are usually contained in secure retention ponds for separation and recovery of any heavy metals or other pollutants. Uranium mill tailings are also associated with increased concentrations of toxic metals, which are a key source of surface and groundwater contamination. The recycled water undergoes natural evaporation or is pumped back to the milling process.

1.2.2.3 Nuclear Power Plants

The gravest introduction gateway of radioactive pollutants is through accidents or incidents from nuclear facility. After the historical Hiroshima and Nagasaki nuclear bomb disaster and atmospheric nuclear weapon tests in the 1950s and 1960s, three more accidents have been witnessed at Mile Island in the USA (1977), the 1986 Chernobyl disaster, and tsunami induced destruction of Fukushima Japan 2011 (Zheng et al. 2013). The operation of these plants is not excepted from generating waste materials which find their way into the environment. The major radioactive wastes include uranium mill tailings, used reactor fuel, and other radioactive residues (Campbell et al. 2015). These materials remain radioactive, and they are hazardous to human health because their disintegration takes thousands of years. The waste is classified as high-level or low-level waste. High-level radioactive waste comprises of spent nuclear reactor fuel (Nagasaki et al. 1998). The radioactivity of nuclear waste reduces with time through radioactive decay to generate different daughter nuclides. The time taken for the radioactivity to decrease to half its original level is called the half-life ($t_{1/2}$). Short-lived radioactive wastes with shorter half-life are briefly stockpiled to diminish potential radiation health and environmental risk before discarding. Low-level radioactive waste includes tools and equipment, protective wear, and other disposable items which accumulate radioactive dust or particles within the plant premises. Because of their potential to pollute the external environment, they must be handled, stored, and disposed in a safe way (Poškas et al. 2019).

1.2.2.4 Radioactive Elements in Medical Applications

Naturally occurring radionuclides are rarely used in medical applications. Artificially made RNs used in healthcare are generated in nuclear reactors, charged particle accelerators, and radionuclide generator devices (Venkatesh and Kang 2021). Radioisotopes in medicine are particularly used in the diagnosis and treatment of disease. Radiolabelled compounds are used for in vivo imaging and therapeutic applications, and these radiopharmaceuticals (e.g., peptides, antibodies, and complexes) are administered in low concentrations, at which they do not exhibit any pharmacological effect. The two imaging techniques used are single-photon emission computed tomography (SPECT) where organ images are acquired and positron emission tomography (PET) which visualizes the metabolic biochemical transformation in the cells after administering a radiolabeled tracer. The metal complexes commonly used as radiopharmaceuticals in SPECT and PET include compounds of ^{99}Tc, ^{111}In, ^{201}Tl, ^{67}Ga, ^{68}Ga, ^{123}I, ^{131}I, ^{51}Cr, ^{35}S, ^{32}P, and ^{18}F (Venkatesh and Kang 2021). In therapy, radiation is applied to targeted organs by using either a theragnostic radionuclide that releases both therapeutic (e.g., α or β^-) and diagnostic (e.g., γ or positron) radiations or bi-radionuclide systems with one responsible for imaging while the other is for therapy (Tan et al. 2020). A typical model is ^{131}I which is supplied as NaI in the management of thyroid cancer. ^{131}I discharges β-particles and γ-radiation for therapeutic and diagnostic purposes, respectively, and it is target delivered to the thyroid cells, with insignificant uptake or effect on the other body cells. However, cumulative accumulation of radiation dose to radiology patients and occupational staff presents a potential health risk in the long term (Adliene et al. 2020).

1.2.2.5 Effect of Radionuclides on Environmental and Human Health

The exploration, mining, processing, and waste management of uranium can impact groundwater in several ways. Contamination can arise from the surface via infiltration of contaminated surface water, waste dumps, tailings, and airborne particles from above or from beneath the water table (Duggal and Sharma 2017). All naturally occurring radionuclides emit α-, β-, and γ-radiation, but the α-particles are the prime radiation hazard. Ionizing radiation mainly induces DNA damage through direct and indirect mechanisms ultimately leading to onset of various cancers (Miller et al. 2002). Uranium usually exhibit dual toxicities, chemo- and radiotoxicity, due to heavy metal and radionuclide properties, respectively (Rump et al. 2019). Chemotoxicity mechanisms include cytotoxicity, oxidative stress, genotoxicity, and apoptosis usually at elevated concentrations (Shaki et al. 2013).

Most countries have compulsory imposed environmental laws and regulations, which prohibit direct introduction of uranium mine wastewater into the environment. Radiation exposure can be classified as internal or external and can be assimilated via various exposure pathways. The food and water consumption are the primary internal source of human exposure to radionuclides (Bosshard et al. 1992). However, due to ubiquitous existence in the ecosystem, individuals are exposed to other routes such as inhalation and external dermal contact. However, patients subjected to radiological radiation together with radiological staff and personnel working in mining and nuclear industries are at higher risk than the general public (Watson et al. 2005). Radionuclides are also distributed in the aquatic system. A systematic study by Oura and Ebihara (2012) determined the radioactive levels of three nuclides (^{131}I, ^{134}Cs, and ^{137}Cs) in three rivers following the Fukushima Daiichi Nuclear Power Plant accident. Higher concentrations were reported for all radioisotopes, which, however, decrease with time. Radionuclides also accumulate in aquatic plants and sediment. Environmental samples from a lake polluted with radioactive waste showed higher activities of ^{90}Sr (Taylor et al. 2007). Activities of 0.1 pg/g (0.5 Bq/g), 0.04 pg/g (0.2 Bq/g), and 3 pg/L (5 Bq/L) were observed for geological sediments and aquatic plant and water samples, respectively.

A previous study investigated possible health consequences from exposures to radionuclides released from coal-fired brick kilns (Abedin et al. 2020). The ash emission to neighboring atmosphere showed that the air absorbed dose rate was beyond the world recommended kilns chimney average permissible emission values (55 nGy/h). Epidemiology studies in occupational nuclear plant workers exposed to prolonged low to medium doses of radiation have shown higher risks of cancer parallel to non-cancer diseases, e.g., cataracts and cardiovascular diseases (Ivanov et al. 2006, 2008, 2012). Epidemiology studies have concluded that one exposure experience can intensify cancer risk for life; numerous small exposures can increase cell proliferation risk; the younger generation is more prone than the old; unborn babies are more vulnerable than children; females are more disposed than males; and risks vary by organ or tissue (Boice 2011).

1.3 Bioremediation of Metal(loid)s and Radionuclides

Relative to organic pollutants, toxic metals are regarded as persistent in environmental systems since they are nonbiodegradable and, thus, cannot be easily broken down (Alotaibi et al. 2021). Specifically, metal(loid)s and radionuclides pose environmental and human health risks and have to be removed from the environment. To achieve this, a number of methods including chemical, physical, and bioremediation techniques have been investigated (Ayangbenro and Babalola 2018; Corral-Bobadilla et al. 2019; Alotaibi et al. 2021). Chemical methods include chemical precipitation, while electrocoagulation, evaporation, membrane filtration, and solvent extraction are examples of physical methods (Fig. 1.2) (Araya et al. 2021). Toxic metals removed using physical techniques require further processing, increasing costs and compromising specificity. Chemical approaches are also used to modify the chemistry of toxic metals, subsequently decreasing their toxicity (Alotaibi et al. 2021). Although methods such as encapsulation, extraction, precipitation, immobilization, ion exchange, and leaching are efficient at large scale, their major setback is the generation of byproducts, which exerts a requirement of additional processes downstream. Despite being effective, most of these methods are not eco-friendly, cheap, or feasible, making their use a challenge. As a result, alternative techniques are required for the remediation of toxic metals.

The bioremediation process uses animals, plants, and microorganisms to remove pollutants such as toxic metals from contaminated aquatic systems (Ayangbenro and Babalola 2018; Alotaibi et al. 2021). Bioremediation is preferable because it is noninvasive, economically feasible, less water-intensive, easy to implement, and unselective, generates less sludge, and is very efficient. In addition, a wide variety of materials and biological species are available (Araya et al. 2021; Darham et al. 2021; deWet and Brink 2021). A number of bioremediation approaches, some of which have been integrated with other techniques, have been investigated for the removal of metal(loid)s and radionuclides from aquatic environments. The major bioremediation forms are biosorption, mycoremediation, phycoremediation, and phytoremediation (Fig. 1.2) (deWet and Brink 2021). In addition, bioremediation

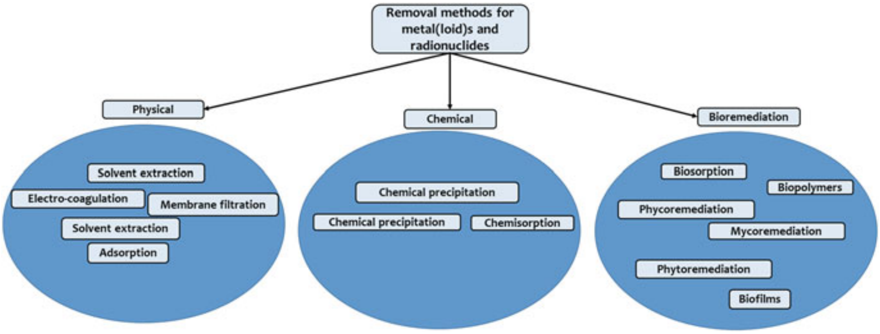

Fig. 1.2 Removal methods for metal(loid)s and radionuclides in aquatic systems

using bacterial species such as *Bacillus* spp., *Escherichia coli*, and *Arthrobacter* is gaining prominence in the removal of different toxic metals in the aquatic environment due to their environmental friendliness and high efficacy (Alotaibi et al. 2021; González et al. 2021).

1.3.1 Biosorption

Owing to process flexibility and low cost, adsorption using biomass-derived materials is widely used in toxic metal remediation. As a result, various adsorbents with high adsorption capacity have been explored for the removal of toxic metals from aquatic systems (Corral-Bobadilla et al. 2019). Feedstock for adsorbents include agro-wastes, industrial biowastes, and municipal biosolids, making the resulting adsorbents low-cost. Such low-cost adsorbents have environmental and economic advantages. Microorganisms can also achieve bioremediation through biosorption mechanisms.

1.3.2 Mycoremediation

Mycoremediation is bioremediation using fungi. Fungi produce numerous metabolites, which are easily propagated and are excellent remediators. The mechanisms of mycoremediation include physisorption on mycelium filaments (deWet and Brink 2021). Previous studies investigating toxic metal removal have identified adsorption on hyphae surfaces as the principal removal mechanism for *Aspergillus* genus fungi (deWet and Brink 2021). A summary of metal(loid)s degraded by fungi is presented in Table 1.2.

Fungi are suitable for remediation due to their robust growth, large aspect ratio, tolerance to toxic metals, habituation to varying pH and temperature, and possession of metal-binding proteins (Singh et al. 2015; Khan et al. 2019a, b). The fungi can employ ligninolytic and antioxidant enzymes in adapting to oxidative stress during the breakdown of the metal(loid)s and radionuclides (Tchounwou et al. 2012; Chibuike and Obiora 2014; Singh et al. 2015). The primary mechanisms for the

Table 1.2 Examples of fungi used to degrade metal(loid)s

Fungi	Metal(loid)s	References
Aspergillus, *Rhizomucor*, *Fusarium*, *Emericella*	As	Singh et al. (2015)
Funneliformis geosporum	Zn	Abu-Elsaoud et al. (2017)
Pleurotus ostreatus	Pb, Zn, Cr, Co, Cu, Ni	Vaseem et al. (2017)
Fomitopsis meliae, *Absidia cylindrospora*, *Rhizopus microsporus, Trichoderma ghanense*	Cu, As, Cd, Pb, Fe	Oladipo et al. (2018), Albert et al. (2018)
Aspergillus species	Pb, Hg	Khan et al. (2019a, b)
Penicillium rubens	Cd, Cr	Khan et al. (2019a, b)

breakdown of metal(loid)s by fungi are biosorption, bioaccumulation, and biovolatilization (Table 1.2) (Igiri et al. 2018; Boriová et al. 2014; Fomina and Gadd 2014).

1.3.3 Phycoremediation

The use of cyanobacteria, microalgae, and macroalgae to remove or biotransform toxic metals in aquatic systems is called phycoremediation. Owing to its rapid kinetics, high efficiency, and abundant resources, this approach offers economic and ecological benefits (Aranguren Díaz et al. 2022). The main limitation of bioremediation using microalgae is the harvesting, haulage, and disposal of spent material. The key strategies used by microalgae for toxic metal removal present benefits relative to other biological techniques that use microorganisms. The mechanisms involve biosorption, which is a passive process that immobilizes pollutants via electrostatic interactions of the toxic metals with the cell wall and the extracellular matrix. For instance, because of the surface properties of microalgae and retention capacity, the biomass can adsorb Cr(VI) in aquatic systems (Aranguren Díaz et al. 2022). A previous study achieved 97.15% Pb and 97.48% Cd removal using *Eichhornia* sp. (Monsef et al. 2014), while another study removed 75% Cd and 95% Pb using *Porphyra leucosticta* (Ye et al. 2015). Removals for Zn (56.4%), Cd (40.2%), and Cu (29.1%) using *Oscillatoria* sp. were modest (Kahashan and Kadhim 2018). These results were comparable to the removals using *Westiellopsis prolifica* and *Stigonema* sp. (Kahashan and Kadhim 2018).

1.3.4 Microbial Bioremediation

Microbial bioremediation, especially the application of bacteria, has attracted research attention owing to its practicability and high efficiency (Alotaibi et al. 2021). Bacteria remove toxic metals via several mechanisms such as adsorption, bioaccumulation, biosorption, and efflux and resistance mechanisms (Ghimire and McCarthy 2018). While biosorption is the removal of toxic metals through passive interaction with dead biomass in aqueous media, the bioaccumulation process is active and requires the metabolism of living organisms (Ghimire and McCarthy 2018). Overall, microorganism-mediated reduction or sequestration of toxic metals is a more effective and efficient option, even at low concentrations. Examples of microorganisms used for the sequestration of toxic metals include bacteria such as *Arthrobacter*, *Bacillus*, *Escherichia coli*, *Flavobacterium*, and *Pseudomonas*, yeast such as *Candida utilis* and *Candida maltosa*, and fungi such as *Aspergillus* sp., *Hypocrea tawa*, and *Penicillium* sp. (Alotaibi et al. 2021; González et al. 2021).

Bacteria are ubiquitous in the environment, and their geometry and morphological diversity, along with resistance mechanisms, suit them for bioremediation of toxic metal-contaminated waters. Consequently, various species of bacteria have been explored in the removal of toxic metals such as Cd, Cr, Cu, Hg, Ni, and Zn from aquatic environments (Ayangbenro and Babalola 2018). Because many bacterial species have adapted to develop mechanisms which facilitate resistance to bioremediate toxic metals even at elevated concentrations, bacteria-based biosorption has the advantages of being economically feasible and inexpensive (Alotaibi et al. 2021). Hence, microbial processes that mediate the detoxification and immobilization of metal(loid)s through resistant microbial strains can remove metal(loid)s from aquatic systems (Ayangbenro and Babalola 2018). Bacteria can also sequestrate toxic metals via the formation of extracellular polymeric substances or biofilms.

1.3.5 Biopolymers and Biofilms for Toxic Metal Removal

Extracellular polymeric substances from bacteria can significantly influence biosorption. Besides bacteria, some algae and fungi produce exopolysaccharides, which comprise mainly of polysaccharides but can also carry proteins, phospholipids, and nucleic acids. Polysaccharides can be attached to the cell surface of the microorganism or released into aquatic systems (Ghimire and McCarthy 2018). Biopolymers can withstand a broad range of pH and temperature and can influence the properties of interfaces. For instance, pH influences the functional groups available to interact with metal(loid)s, thus providing varying active sites on the organism surface at different pH. Under alkaline conditions, the concentration of H^+ is low; therefore, there is less competition with metal(loid)s for biopolymer reactive sites. Under a neutral environment, the functional groups carry a negative charge and can interact with metal cations to form stable organometallic complexes. High temperatures favor biopolymer-metal adsorption, and the affinity for active sites increases with increasing temperature, facilitating the metal cations and the functional groups of the biopolymer to have direct contact. Extreme temperatures can, however, impair the biopolymer structure and damage some functional groups, resulting in a reduction in efficiency. Overall, the metal binding ability of the biopolymers is affected by the characteristics of the biomass, affinity and specificity toward the targeted toxic metals, temperature and pH of the contaminated medium, hydrodynamics of the biopolymer and toxic metal ions, and available functional groups (Ayangbenro and Babalola 2018). The biopolymer surface functional groups have different selectivities and affinities for metal(loid) ions. For instance, phosphate and carboxyl groups are the major groups that bind toxic metal ions and are more effective under neutral pH conditions. Owing to high pKa values, amides, nucleic acids, and hydroxyl groups have weaker binding ability relative to phosphate and carboxyl groups (Ayangbenro and Babalola 2018).

Microbial substances can also serve as flocculants in separating suspended solid-liquid. Generally, the flocculation mechanism is initiated by colloid aggregation resulting in floc formation. Inorganic flocculants are limited by potential toxicity and the generation of large volumes of sludge and are nonbiodegradable. Consequently, there is scope for using polymers produced from bacterial activity as bioflocculants since they are eco-friendly and non-toxic, do not result in secondary pollution, and are effective in removing toxic metals and suspended solids from aquatic systems (Ayangbenro and Babalola 2018). Bioflocculants are intricate macromolecular polyelectrolyte mixtures produced by various organisms, and they carry numerous organic acid moieties like glutamic, aspartic, glucuronic, galacturonic, and uronic acids (Ayangbenro and Babalola 2018). These functional groups confer the bioflocculants' metal(loid) removal capacity. Overall, bioflocculants are versatile, cost-effective, and eco-friendly and can effectively remediate toxic metals.

Bacterial colonies accumulate at interfaces forming cell mass and manifest in flocs, mats, sludge, and biofilms. They can form from individual or a number of species of organisms comprising of protozoa, fungi, bacteria, and algae. Biofilms are stable, very structured ecosystem commonly surrounded by a matrix attached to some surface. They are resistant to antibiotics, disinfectants, severe oxygen concentrations and pH, and toxic metal ions (Ayangbenro and Babalola 2018). The advantages of biofilms include nutrient availability, persistence in a range of metabolic configurations, and communication and exchange of genetic material. Biofilm-based toxic metal removal is vital because high metal concentrations are harmful to planktonic communities. Biofilms increase the tolerance of microorganisms to toxic metals and acidic conditions, owing to improved adaptation and survival since the matrix provides protection. The macromolecules within the biofilm matrix exhibit properties such as hydrogen bonding, London forces, and electrostatic interactions, which are influential in the sorption of toxic metals. Toxic metal tolerance and removal are also enhanced by the closeness within the biofilm and the physiological exchanges among the organisms (Ayangbenro and Babalola 2018).

1.4 Conclusion

Metal(loid)s and radionuclides occur in the environment mainly as a result of human activities. These toxicants are persistent in the environment and bioaccumulate up the food chain to humans. Therefore, they pose a number of environmental and human health risks. In addition to being toxic, radionuclides emit radioactivity that is carcinogenic. Consequently, the removal of metal(loid)s and radionuclides from environmental compartments such as aquatic systems is imperative. To achieve this, a range of chemical, physical, and bioremediation strategies have been explored. Of these methods, bioremediation provides benefits of economic feasibility and environmental friendliness. Various bioremediation techniques are available, and the use of plants, animals, and microorganisms is attractive because of high efficiency and eco-friendliness. Further work should, thus, focus on the application of a wider range of microorganisms for toxic metal remediation.

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2

Environmental Pollutants: Organic and Emerging Contaminants

Deborah T. Ruziwa, Desmond D. Rutsito, and Nhamo Chaukura

Abstract

Environmental contamination by organic and emerging contaminants emanating from anthropic activities is widespread globally. Such activities include agrochemical, pharmaceutical, textile, and petroleum manufacturing industries. The contaminants may bioaccumulate in food and environmental compartments such as aquatic systems. Some pollutants, for example, hydrocarbons, can volatilize from soil, vegetation, and aquatic environments into the atmosphere, where they are mobilized for considerable distances before redeposition. Chlorinated compounds are used to make drinking water disinfectants, pesticides, pharmaceuticals, and other industrial applications. Due to extensive agricultural activities around the world, pesticides were ubiquitous and are commonly detected at low concentrations. Other pollutants include explosives, which contain toxic and mutagenic xenobiotics, endocrine-disrupting chemicals, polyfluorinated compounds, and pharmaceutically active compounds. All these contaminants cause unfavourable environmental and human health effects and so should be removed from aquatic systems.

Keywords

Carcinogenic · Endocrine disruptors · Pesticides · Pharmaceutically active · Polycyclic aromatic hydrocarbons

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2.1 Introduction

Contamination of the environment by persistent organic pollutants (POPs) and emerging pollutants (EPs) generated from human activities is prevalent around the world. Emerging pollutants and synthetic organic contaminants are generated from pharmaceutical, agrochemical, textile, and petroleum industries and wastewater treatment processes (Chaukura et al. 2016a, b). EPs are substances which are not routinely reported or monitored in the environment and have no regulations to control them (Chaukura et al. 2016a, b; Egbuna et al. 2021), and they include personal care products (PPCPs), recreational drugs, analgesics, and many other pollutants whose environmental and human risks are yet not extensively studied (United Nations Conference on Trade and Development 2011). POPs are a significant class of organic contaminants, and these include industrial chemicals such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) (Yadav et al. 2015). There are numerous categories of organic and emerging contaminants, and these include hydrocarbons and polycyclic aromatic compounds, chlorinated compounds, petroleum hydrocarbons, fertilizer and pesticides, and explosives (Fig. 2.1).

This chapter discusses the occurrence and health impacts of organic and emerging pollutants. It sets the tone for subsequent chapters that explore the various remediation strategies used for the remediation of organic and emerging contaminants from contaminated aquatic systems.

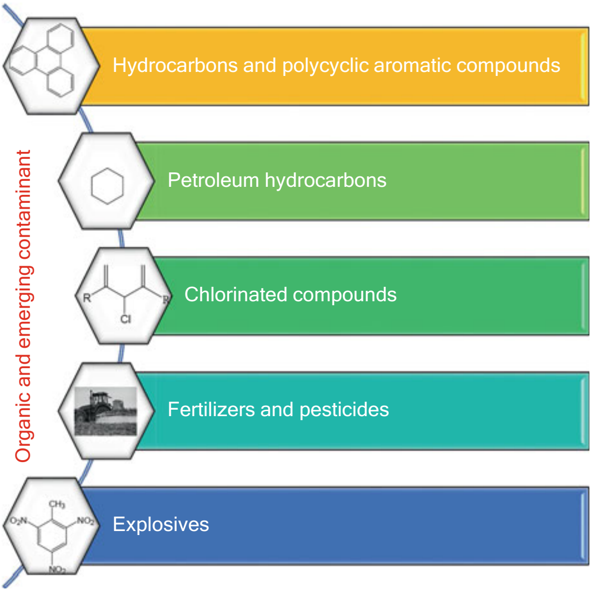

Fig. 2.1 Different classes of organic and emerging contaminants

2.2 Organic Pollutants

This section deals with organic pollutants, and these organic pollutants are classified as hydrocarbons, polycyclic aromatic hydrocarbons, chlorinated organic compounds, petroleum hydrocarbons, fertilizers, pesticides, and explosives. The section discusses the physicochemical properties of the organic compounds, their potential sources, and occurrences.

2.2.1 Hydrocarbons and Polycyclic Aromatic Hydrocarbons

Hydrocarbon pollutants are typically lipophilic and hydrophobic. In aquatic media and soils, they have a high affinity for organic matter than on aqueous media. Hydrocarbons also partition onto lipids in organisms and are stored in fatty tissue. Hydrocarbons may therefore accumulate in food chains. Hydrocarbon pollutants tend to volatilize from soil, water systems, and vegetation into the atmosphere where they are transported for long distances before being redeposited. Hydrocarbon pollutants are resistant to breakdown reactions in the air (Purcaro et al. 2013).

PAHs have two or more condensed aromatic rings. Previous researchers reported that PAHs are produced when organic matter is combusted at 700 °C. PAHs consist of condensed aromatic rings derived from oil spills, volcanic eruptions, and the incomplete combustion of biomass and fossil fuels, and are more concentrated in urban areas. Other important sources of PAHs include production of asphalt, incineration, coal tar, industrial power generation, coke, catalytic cracking, and petroleum and aluminium production. The highest concentrations of PAHs in the atmosphere occur in urban areas as a result of increased automobile traffic and dispersion of atmospheric pollutants (Srogi 2007a, b; Purcaro et al. 2013; Singh et al. 2016).

PAHs often occur as a mixture of compounds in the environment. USEPA listed the following 16 PAH compounds as hazardous substances: anthracene, acenaphthylene, acenaphthene, benzanthracene, benzo[b]fluoranthene, benzo[a] anthracene, benzopyrene, benzoperylene, chrysene, dibenzoanthracene, fluorine, fluoranthene, naphthalene, indenopyrene, phenanthrene, and pyrene. PAHs comprising two or three rings include acenaphthene, anthracene, naphthalene, and phenanthrene, while PAHs with five or more rings include perylene, benzo[a]pyrene, and coronene (Singh et al. 2016).

The environmental fate of PAHs depends on their physicochemical characteristics. Non-polarity and hydrophobic properties of PAHs are responsible for their environmental persistence. PAHs are hydrophobic; therefore, they tend to be rapidly absorbed by sediment and soil. Various PAHs are relatively less soluble in water but are highly lipophilic. On exposure to solar radiation ultraviolet light, PAHs may be photodecomposed. PAHs may act with atmospheric pollutants such as sulphur dioxide, nitrogen oxides, and ozone yielding sulphonic acids, nitro and dinitro oxides, and diones (Srogi 2007a, b).

2.2.2 Chlorinated Compounds

A large amount of chlorinated compounds are manufactured for agricultural, commercial, and industrial purposes. Approximately 15,000 chlorinated organic compounds are used in the manufacture of pharmaceuticals, pesticides, and drinking water disinfectants (Arjoon et al. 2013). Chlorinated organic compounds are used for controlling mosquitoes, termites, weeds, and many types of insects. Dichlorodiphenyltrichloroethane (DDT) is widely used in controlling mosquitoes and snails that cause malaria and bilharzia, respectively (Jovanni et al. 2010). DDT, aldrin, and dieldrin are restricted because of their persistence and toxic effects on wildlife (Stevens et al. 2003). Chlorinated compounds enter aquatic systems as industrial effluents, farm run-off, soil erosion, and sewage run-off (Ssebugere et al. 2013, 2014). Water is a major transporter of chlorinated compounds from point sources to other areas within the environment. Chlorinated compounds are discharged into water systems through run-off from non-point soil sources (Aly Salem et al. 2013). High concentrations of chlorinated compounds have been detected in streams traversing agricultural fields. Occurrence of chlorinated compounds in sediments of different aquatic matrices has been reported. Organic contaminants such as PCBs and hexachlorobenzenes (HCBs) have been shown to be present in various samples (Williams 2013; Olutona et al. 2016). Varying concentrations of chlorinated compounds in sediments, water, and aquatic organisms have been reported. The lowest concentration of chlorinated compounds was reported in water samples, while the highest concentration was reported in fish. Biomagnification and bioaccumulation were reportedly responsible for the presence of chlorinated compounds in water and fish, since the compounds biomagnify up the food chain and are not readily metabolized (Olutona et al. 2016).

2.2.3 Petroleum Hydrocarbons

Sources of petroleum hydrocarbons (PHs) include crude oil distillates such as diesel, petrol, oil, and lubricants. Petroleum compounds exist as mixtures of solid, liquid, and gaseous hydrocarbons with small quantities of sulphur, oxygen, and nitrogen-containing compounds and trace quantities of metals (Speight 2015). PHs are classified as paraffin, cycloparaffins, and aromatics. Paraffin is composed of saturated hydrocarbons with linear or branched carbon chains, while cycloparaffins are saturated hydrocarbons with at least a ring moiety and a paraffin side chain. Aromatics have one or more aromatic moiety connected to substituted rings or a paraffin side chain (Logeshwaran et al. 2018). As pollutants, PHs are categorized as emerging pollutants and xenobiotics. When discharged into aquatic environment, the lighter PHs tend to float on the water surface forming a thin surface film, and heavier PHs settle at the bottom in the sediment. When PHs are discharged in soil, different compounds detach from the primary mixture and percolate through the soil in groundwater (Al-Majed et al. 2012; Souza et al. 2014). High molecular weight PHs are less mobile and usually trapped in their pure liquid form in soil pores and are absorbed by clay soil and pose as a source of groundwater contamination (Logeshwaran et al. 2018). Due to their bio-persistence and structural complexities, PHs are priority environmental pollutants.

2.2.4 Fertilizer and Pesticides

Pesticides are chemical substances capable of incapacitating and killing pests (Asghar and Malik 2016). Pesticides at low concentration cause water pollution that may result in a serious threat to the environment (Agrawal et al. 2010). In surface water, pesticides are mostly detected at low concentrations of μg/L and were ubiquitous at all sampling sites (Peng et al. 2018; Sun et al. 2018; Köck-Schulmeyer et al. 2021). Despite dilution from rainfall, water samples collected in the rainy season had higher pesticide concentrations due to surface run-off (Sun et al. 2018). Prolonged exposure to pesticides (e.g. aldrin, hexachlorobenzene, chlordecone, pentachlorobenzene) may inhibit cholinesterase enzymes, increase the risks of developing cancer and neurodegenerative diseases, and can affect the female reproductive system by causing ovarian disorders, depressing fertility, spontaneous abortion, premature birth, low birth weight, growth anomalies, and endocrine disruption (Singh et al. 2011; Asghar and Malik 2016; Rani et al. 2017). Intensive crop farming may cause extensive leaching of nitrogen into the environment. Nitrogen leaching results in extensive deoxidation of water reserves and reduces the quality of groundwater. Loss of nitrogen in agriculture has caused extensive environmental damage to natural terrestrial and aquatic ecosystems (Hansen et al. 2001). Water with high nitrate concentration may immobilize haemoglobin in red blood cells. Organophosphates are associated with acute abdominal pain, headaches, nausea, vomiting, and eye and skin problems (Sharma and Singhvi 2017). Soil and water contamination by toxic agrochemicals such as phosphate fertilizers containing heavy metals is of great concern. The pollutants in water are usually present in small quantities; however, their toxic effects take years to manifest in humans causing chronic kidney diseases (Wimalawansa and Wimalawansa 2015).

2.2.5 Explosives

The most common types of explosives are hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4,6-trinitrotoluene (TNT), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). 3-Nitro-1,2,4-triazol-5one (NTO) is one of the new explosive compounds used in insensitive munitions and was developed to replace TNT and RDX (Fig. 2.2) (Pillard et al. 2017). TNT is a carcinogenic toxicant which remains strongly bound to soil particles, while RDX is extremely mobile and leaches into groundwater posing a risk to potable water supplies (Rylott et al. 2011). NTO creates acidic conditions, and research indicates that the severe toxicity can be ascribed largely to its acidic nature (Pillard et al. 2017). Generally, explosives contain toxic

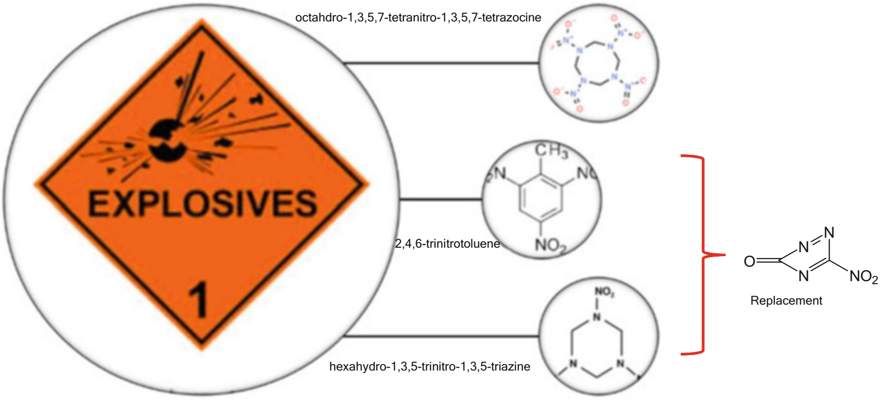

Fig. 2.2 The most common types of explosives

and mutagenic xenobiotics which persist in the environment and are difficult to remove (Chatterjee et al. 2017).

Contamination by explosives is mainly in soils, either arising from manufacturing processes, military operations, open burning/detonation, or inappropriate disposal of munitions (Chatterjee et al. 2017). Once in soil, the explosives are taken up by plants, and TNT readily transforms in plant roots but remains very toxic. Although RDX and HMX remain undegraded in plant tissues, they accumulate in aerial parts of plants (Panz and Miksch 2012). However, previous research has reported that the bioaccumulative potential for RDX and TNT via the food chain is somewhat low (Houston and Lotufo 2005).

Generally, explosives have environmental and health effects which include mortality; RDX and HMX caused mortality of earthworms (Panz et al. 2013), and NTO resulted in death of tadpoles and delays in metamorphosis (Pillard et al. 2017). RDX resulted in inhibited seed germination and an increase in seedling morphological damage, while TNT did not have an effect on both (Via et al. 2015).

Several techniques have been employed to remove explosives from the environment, and the most common are biotechnological approaches like phytoremediation which is cheaper, eco-friendly, and generally accepted by society. The use of genetically modified plants holds great promise, since it combines with the capacity of bacterial genes to detoxify contaminants (Chatterjee et al. 2017). This is in agreement with a research where engineered *Arabidopsis* plants degraded RDX while tolerating the phytotoxicity of TNT (Rylott et al. 2011). Biochar was also found to promote the reductive removal of explosive RDX and 2,4-dinitrotoluene by dithiothreitol (Oh et al. 2012).

2.3 Effect of Organic Contaminants on Environment and Health

PAHs are highly mutagenic and carcinogenic and are mainly adsorbed onto airborne particulate matter. Lower molecular weight compounds have weaker mutagenic and carcinogenic properties, and they are abundantly available in urban atmospheres and react with other contaminants forming toxic compounds (Park et al. 2002; Srogi 2007a, b). PAH particles that affect human health are inhalable with an aerodynamic diameter of less than 2.5 μm. Plants have high surface areas protected by waxes that expedite accumulation of PAHs. The stomata on leaves take up PAHs in gaseous phase. Plants with hairy leaves have been found with higher concentrations of PAHs than non-hairy leaves. According to Grova et al. (2006), food was singled out as the main PAHs intake pathway for humans whose occupations do not expose them to PAHs. These foods include grilled meat, contaminated vegetables, cereals, and flour exposing.

Chlorinated organic compounds are readily absorbed on the digestive system and bioaccumulate in fatty tissue, the brain, breast milk, and adipose tissue. Lengthy exposure to chlorinated organic compounds may damage the liver, kidneys, central nervous system, thyroid, and bladder (Siddharth et al. 2012; Olutona et al. 2016). Blockage of neurotransmitters in the central nervous system leading to headaches, muscle twitching, seizures, nausea, brain excitation, and confusion has been reported to be caused by exposure to higher concentration of heptachlor, heptachlor epoxide, and dieldrin (Loe et al. 2013; Olutona et al. 2016). Chlorinated compounds may also interact with human hormonal systems, and studies have shown that they harm developing embryos, foetus, and toddlers and the compounds are carcinogenic (Arjoon et al. 2013). Groundwater contaminated by chlorinated hydrocarbons has been reported to cause adverse health conditions in humans. Acute symptoms such as eye irritation, diarrhoea, and sleepiness have been documented. Chronic illnesses including cancers of genitourinal organs, respiratory organs, and gastrointestinal organs have been attributed to chlorinated hydrocarbons such as trichloroethylene, perchloroethylene, and vinyl chloride. Kidney damage by chlorinated hydrocarbons is thought to be due to injury to proximal renal tubules and disruption of the kidney immune system (Chen and Wu 2017). Epidemiological studies on Taiwanese residents living close to petrochemical industries have shown that chlorinated hydrocarbons cause renal damage (Calvert et al. 2011).

Once PHs have been emitted into the environment, components of the petroleum hydrocarbons partition between the oil, air, soil, and water phases. When discharged in water, the behaviour and fate of the petroleum hydrocarbons are largely determined by their composition. Biological, chemical, and physical processes determine the ageing of spilled oils resulting in changes in their complexity and composition. Generally high molecular weight PHs have high toxicity, and vice versa. In this regard, light cyclic alkanes are more toxic to aquatic organisms compared to aromatic and aliphatic compounds with similar molecular weight. Levels of environmental contamination due to PHs are generally difficult to quantify because of their nature and sources of contamination. PHs have toxic, mutagenic, and

Table 2.1 Effects of emerging organic pollutants on environment and human health

Environmental pollutant	Effect on environment and human health
Hydrocarbons	
Polycyclic aromatic hydrocarbons	Mutagenic and carcinogenic
Chlorinated organic compounds	Damage the liver, kidneys, CNS, thyroid, and bladder. The compounds are carcinogenic and harm embryos, foetus, and toddlers
Petroleum hydrocarbons	Mutagenic and carcinogenic effects. Exposure to high concentrations may lead to death
Fertilizers and pesticides	Prolonged exposure can inhibit cholinesterase enzymes and increase risk of cancer and neurodegenerative diseases. Can cause ovarian disorders, depressing fertility, spontaneous abortion, premature birth, low birth weight, growth anomalies, and endocrine disruption
Explosives	For example, TNT is carcinogenic, toxic, and mutagenic; reported cases include mortality of earthworms, death of tadpoles, delays in metamorphosis, inhibited seed germination, increase in seedling morphological damage
Perfluorochlorinated compounds	Carcinogenicity, immunotoxicity, hepatotoxicity, and reproductive and developmental effects. PFOA caused a reduction in birth weight in humans and rodents and endocrine disruptors, cause membrane damage in the digestive gland, and disrupt the function of the reproductive gland, affecting growth and development of organisms
Pharmaceutically active compounds	Genetic alterations in DNA and genotoxicity in aquatic systems cause liver complications and damage the nervous system

carcinogenic effects in humans when inhaled, ingested, and dermally contacted (HPA 2006; Logeshwaran et al. 2018). Exposure to high concentrations of PH in humans may lead to death. Petroleum hydrocarbons in aqueous medium may disrupt cell membranes of invertebrates and microbes, and normal cell functions such as fluidity and integrity are adversely affected. PH inhibits ammonium monooxygenase through competitive binding by light hydrocarbons, thereby making soil microbes such as nitrifying bacteria more vulnerable to further exposure (Logeshwaran et al. 2018). A summary of some of the environmental and human health effects of emerging organic pollutants are presented in Table 2.1.

2.4 Emerging Contaminants

Emerging contaminants emanate from agrochemical, pharmaceutical, and textile industries (Chaukura et al. 2016a, b), and these include polyfluorinated compounds, pharmaceutically active compounds, and endocrine-disrupting chemicals. Even at concentrations as low as 10^{-9} g/L, emerging organic contaminants can affect human and ecological health. Prolonged exposure to low concentrations of most of these bioactive and environmentally stable pollutants can pose severe risks to environmental and human health (Sun et al. 2018).

Oxidative stress inducers can cause genetic alterations in DNA (Egbuna et al. 2021). Metabolites of some pharmaceuticals are more toxic than the parent molecule (Chopra and Kumar 2020). Bioremediation-based methods are a promising alternative in the removal of EOCs (Chaukura et al. 2016a, b; Chopra and Kumar 2020).

2.4.1 Polyfluorinated Compounds

Perfluoroalkyls are stable synthetic chemicals consisting of a lipophilic/hydrophobic carboxylated chain and a hydrophilic reactive group (Fig. 2.3). The sources of these compounds are in products such as carpets, clothes, coatings for pans, fire-fighting foams, lubricants, Teflon, paints, and paperboard for packaging (Arrieta-Cortes et al. 2017). Perfluorochlorinated compounds (PFAS) can be transported in the environment through atmospheric oxidation of precursors (Ademollo et al. 2021). Perfluorooctane sulfonic acid and perfluorooctanoic acid PFOS and PFOA have been found to be emerging organic micropollutants, and their regulation began in 2009. Despite their regulation, the distribution of fate in freshwater system continues to be high priority owing to the toxicity and persistence in sediment, biota, water, and wastewater.

Perfluoroalkyl compounds have been measured in different environmental matrices including air, sediment, soil, biota, humans, and water. PFOS (perfluorooctane sulfonate) showed an increasing trend globally (Skaar et al. 2019). PFAS were predominant in river water (Choo et al. 2020) and were found in lower concentrations in seawater samples (Skaar et al. 2019). Higher levels of PFAs in wastewater effluents relative to influent implied both formation during the treatment process along with low removal efficiency (Lorenzo et al. 2019). Groundwater and surface waters are the major sinks for PFOS and PFOA (Zareitalabad et al. 2013). The mean concentrations of PFOS in fish and water exceeded the European Union

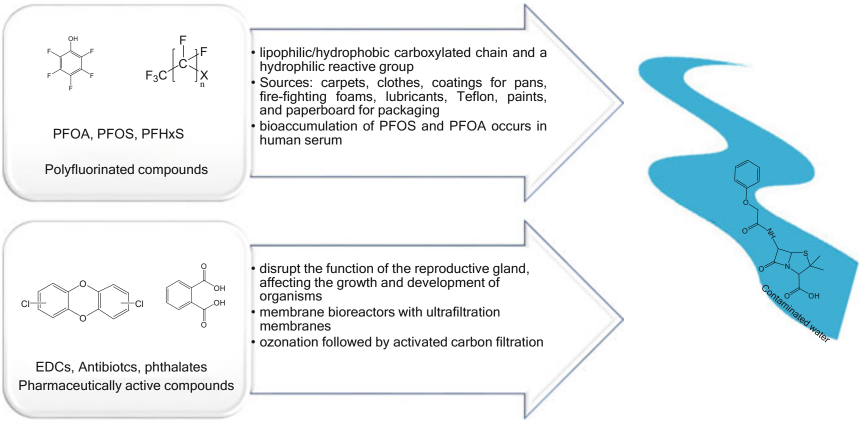

Fig. 2.3 Perfluorinated compounds and pharmaceutically active compounds

environmental quality standards (Lorenzo et al. 2019). Human exposure is primarily via consumption of contaminated drinking water and food and through the inhaling of contaminated air and dust (Zhang et al. 2010). Perfluorinated alkylated compounds (PFAAs) have been detected in dairy products at sub-ppb levels, and this was attributed to the fluorinated polymer material coating the packaging (Still et al. 2013). The bioaccumulation of PFOS and PFOA occurs in human serum with a half-life of 5.4 years and 3.8 years, respectively (Olsen et al. 2007).

PFASs are exceedingly persistent in the environment since they carry both hydrophilic moieties and hydrophobic fluorine-saturated carbon chains as well as being oleophobic (Eke et al. 2020). The environmental stability, non-biodegradability, persistence, and bioaccumulation of PFOS and its associated products have led to increased concerns over the body burden in animals and humans (Lau et al. 2007). Previous researches showed that neither ozonation, sand filtration, nor peroxidation eliminated both perfluorinated compounds, and advanced treatments like reverse osmosis were more effective compared to reverse electrolysis. Granular activated carbon had an average removal efficiency of 45 ± 19% and 64 ± 11% for PFOA and PFOS, respectively (Flores et al. 2013). There is an inherent resistance of PFAS compounds to biodegradation, and this makes it imperative to develop advanced techniques for the removal of these pollutants (Gomez-Ruiz et al. 2018; Trojanowicz et al. 2018). Such techniques include photocatalysis, electrochemical decomposition, and electrocoagulation with an air-cathode. For instance, PFOA was decomposed by nanostructured porous microspheres of In_2O_3 (Li et al. 2013). In_2O_3 materials with higher oxygen vacancy defects showed better activity 74.7 times as fast as P25 TiO_2. Using a composite catalyst derived from TiO_2 and reduced graphene oxide, a 93±7% degradation rate of PFOA was achieved after 12 h. The liberation of fluoride and the generation of shorter-chain perfluorocarboxylic acids were gradually excluded via photogenerated hydroxyl radicals (Gomez-Ruiz et al. 2018).

PFOA were able to be degraded by an electrochemical decomposition in aqueous solution over Ti/SnO_2-Sb/MnO_2, Ti/SnO_2-Sb/PbO_2, and Ti/SnO_2-Sb and gave degradation of 31.7%, 91.1%, and 90.3%, respectively (Lin et al. 2012). However, intermediate products including perfluorocarbons and short-chain perfluorinated carboxylic acids were identified by electrospray ionization mass spectroscopy. PFOS was removed better than PFOA using electrocoagulation with air-cathode because it has higher hydrophobicity (Mu et al. 2021). Recently, a bacterium was used to biodegrade PFOS and PFOA with corresponding formation of fluoride (Huang and Jaffe 2019).

Nanocomposite membranes treated with ultraviolet and liquid aerobic oxidation achieved 99% rejection of PFOA with 99% removal from the PFOA that accumulated on the membrane surface (Eke et al. 2020). Biosorption is attractive for removing these organic contaminants in developing countries because of (1) the abundance of biowastes for use as biosorbent feedstock and (2) poor water and wastewater treatment facilities and (3) this is cheaper than advanced methods (Chaukura et al. 2016a, b).

2.4.2 Pharmaceutically Active Compounds

Pharmaceutically active compounds occur in wastewater, groundwater, and surface water (Bueno et al. 2012; Chopra and Kumar 2020; Deng et al. 2021; Hube and Wu 2021). A footprint of the extensive urban pollution was evident from the prevalence of PPCPs in the aquatic systems (Köck-Schulmeyer et al. 2021). These pollutants can be removed from wastewater by a soil aquifer treatment system although others like carbamazepine remained persistent (Sopilniak et al. 2018). A similar study showed that bacterial biodiversity in activated sludge can decompose pharmaceuticals (Pacholak et al. 2020).

Bio-based removal of these emerging pollutants was achieved by duckweed, which dynamically enhanced the removal of ibuprofen, fluoxetine, 2,4-dichlorophenoxyacetic acid, and triclosan (Reinhold et al. 2010). The active plant processes enhanced microbiological degradation of ibuprofen, uptake of fluoxetine, and removal of transformation products of triclosan and 2,4-dichlorophenoxyacetic acid. Passive plant processes, especially sorption, contributed to the sorption of triclosan and fluoxetine. A separate study used plant presence (*Typha angustifolia* and *Phragmites australis*) which improved the sorption of organic matter along with some PPCPs (Hijosa-Valsero et al. 2011). Yet another study showed that ozone could sequester PPCPs from biologically treated wastewater (Antoniou et al. 2013).

The most widely investigated technologies in removal of pharmaceuticals are membrane bioreactors fitted with ultrafiltration membranes in the secondary step and ozonation followed by activated carbon filtration in the polishing step (Verlicchi et al. 2015). Research showed that algal treatment process enables simultaneous elimination of micropollutants and nutrient recovery from wastewater (Wilt et al. 2016). Because they provide plentiful active sites and oxygenated moieties which facilitate binding, biochar nanoparticles have been used to remove EOCs from wastewater (Ahmaruzzaman 2021). With the rapid development of technologies such as nanosensors, the detection of pharmaceuticals will be rapid, resulting in more efficient removal (Chopra and Kumar 2020).

2.5 Effect of Emerging Contaminant on Environment and Health

Exposure to PFAS compounds is related to a range of adverse health effects (He et al. 2018). Previous studies suggest multiple toxicities associated with PFOS such as carcinogenicity, immunotoxicity, hepatotoxicity, and reproductive and developmental effects (Wang et al. 2010). Most of the studies on health effects of these emerging contaminants to humans have been epidemiological studies which mainly reflected associations between exposure and the health effect.

A report on the association between the in vivo gene expression involved in the metabolism of cholesterol and exposure to PFOA or PFAS indicated that exposure to these compounds may result in a hypercholesterolaemic environment, with broader human health repercussions (Fletcher et al. 2013). Studies showed a strong positive association in men, while in women, no significant correlation was observed between serum PFOA and the prevalence of diabetes (He et al. 2018). An epidemiological study showed there was a correlation between exposure to PFOS and the occurrence of bladder cancer (Alexander and Olsen 2007). In another study, PFOS exposure seemed to be more correlated with cirrhosis than hepatocellular carcinoma, and they discovered a weak correlation between PFOS exposure and liver cancer (Yeung et al. 2013). Further studies concluded that the cancer risk for PFOS is not carcinogenic in humans (Arrieta-Cortes et al. 2017). Other evidence suggested that PFOS and PFOA cause a reduction in birth weight in humans and rodents (Negri et al. 2016). In addition, polyfluorinated compounds are also reported to be associated with adult hearing disturbance (Shiue 2012).

Some PFOS and PFOA are endocrine disruptors. For instance, selected PFOS and PFOA boosted the effects of E2 on oestrogen-responsive gene expressing ERK1/2 activation and the growth of the hormone-deprived T47D cells (Sonthithai et al. 2015). Research also demonstrated that PFOS and PFOA induced oxidative stress leading to apoptosis in tilapia hepatocytes (Liu et al. 2007). Another study discovered that hepatocellular hypertrophy was considerably enhanced by PFOA exposure and significantly increased non-neoplastic liver lesions in mice (Filgo et al. 2015). Research shows that pharmaceuticals cause membrane damage in the digestive gland and lipid peroxidation levels increased in mussels (Gonzales-Rey and Berbianno 2012). In vertebrates, pharmaceutically active compounds can disrupt the function of the reproductive gland, affecting the growth and development of organisms (Fig. 2.3) (Diaz-Torres et al. 2013). Antibiotics and PPCPs have been reported to induce genotoxicity in aquatic species; zebra fish embryos and larvae experience genetic toxicity following exposure to triclosan (Paumo et al. 2021).

The incidence of pharmaceuticals such as antibiotics in the environment may aid antibiotic resistance in pathogenic microorganisms (Paumo et al. 2021). This is more pronounced in wastewater treatment facilities where large varieties of antibiotics together with high bacterial loads contribute to antibiotic resistance and release antibiotic-resistant genes to the environment (Berendonk et al. 2015). Microcystin, a common toxin produced by cyanobacteria in natural aquatic systems, can cause liver complications and damage the nervous system if ingested (Rastogi et al. 2014).

2.6 Conclusion

This chapter has demonstrated the widespread occurrence of organic and emerging contaminants in environmental systems. Such contaminants originate from a range of anthropic activities and end up in the environment where they pose health risks. The particular health risks associated with each contaminant depend on its chemistry and class of origin. Overall, organic and emerging contaminants are toxic, mutagenic, and carcinogenic and are recalcitrant to removal in environmental systems. It is therefore important to develop remediation strategies that can remove the contaminants from the environment.

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3

Biosorption, Bioaccumulation and Biodegradation: A Sustainable Approach for Management of Environmental Contaminants

Sudipa Bhadra and Surajbhan Sevda

Abstract

In this era of rapid industrialization, environmental pollution has become a major concern. Various pollutants from fossil and petrochemical sector, from transportation and agricultural sector and from fashion and cosmetics industry are being released into the environment at a non-permissible rate. Conventional methods to treat pollutants and to decrease their content in the environment are neither sustainable nor cost-effective. A much greener and more sustainable approach is required to treat pollutants at their sources as well as at their release point in the environment. Bioremediation technique is an effective solution for the treatment of persistent hazardous pollutants which upon entering into the ecosystem tend to biomagnify at each trophic level. Biosorption, bioaccumulation and biodegradation are all bioremediation techniques that can be used for removal and degradation of both water and soil pollutants without release of any toxic by-products. Though all the above three bioremediation techniques are very useful for pollutant removal, biosorption has an edge over bioaccumulation when it comes to potentially toxic metal recovery, while biodegradation is especially useful for removal and degradation of petroleum hydrocarbons.

Keywords

Bioremediation · Biosorption · Bioaccumulation · Biodegradation · Biosorbent · Potentially toxic metal

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3.1 Introduction

Consequential environmental complications arise when pollutants of organic and inorganic nature are released into water bodies. These polluted waters come from various industries and also from uncontrolled usage of agrochemicals and fossil fuel and dumping of sewage sludge. These pollutants are highly contaminated with dyes, metalloids and heavy metals in non-permissible amounts. Once these pollutants enter the water bodies, they not only contaminate the water sources but also the nearby soil areas; as a result, these pollutants start to biomagnify once they enter the food chains via aquatic and terrestrial fauna and flora, causing a hazardous effect on the organisms of higher trophic levels.

Remediation of these polluted sites by conventional methods is not effective to remove these pollutants completely; thus, biosorption, bioaccumulation and biodegradation are emerging as much greener, cost-effective and efficient alternatives. For these technologies to be fruitfully utilized, a comprehensive knowledge about their capability and effectiveness to remove and degrade inorganic and organic contaminants is really useful. Recent studies have looked into different methods to remove pollutants as well as different biomaterials that can be potential candidates as biosorbents.

Another major section of pollutants is hydrocarbon released from petrochemical industries. These hydrocarbons can also be released into the environment due to manhandling and occasional spillage of oils on land and oceans. Current practices to dispose of these carcinogens and neurotoxic organic pollutants by incineration or burial in landfills are not effective and are also pretty expensive. Therefore, bioremediation by biodegradation of these contaminated sites is a much more effective solution as bioremediation helps to completely mineralize the organic pollutants into carbon dioxide, water, inorganic compounds and cell protein. Various native microbes from water and soil have the capability to biodegrade these hydrocarbon pollutants.

3.2 Probable Candidates for Sustainable Managements of Environmental Contaminants

Sustainable management of water and soil contaminants includes immediate measures that can be applied to remove and degrade these contaminants along with recovery and utilizations of various heavy metals as well as generation of bioelectricity. While wastewater treatment can be effectively accomplished by using new-age technology such as bioelectrochemical systems (BESs), soil bioremediation on the other hand has come up as an effective way to remove and degrade soil contaminants.

Microbial fuel cell (MFC) and a microbial electrolysis cell (MEC) are two main BES technologies that are majorly used for wastewater treatment as well as for production of bioelectricity and recovery of heavy metals. Other BESs that are also widely used are enzymatic biofuel cells (EBCs), microbial reverse-electrodialysis cells (MRECs), microbial desalination cells (MDCs), microbial solar cells (MSCs) and microbial electrosynthesis cells (MESCs).

For soil contaminants, bioremediation techniques such as biopile, windrows, land farming, bioventing, bioslurping, biosparging, phytoremediation, permeable reactive barrier (PRB), biosorption, bioaccumulation and biodegradation are all probable candidates for degrading and removing toxic pollutants from contaminated soil areas.

Among all these techniques, biosorption, bioaccumulation and biodegradation have been elaborately discussed in this article for better understandability of these techniques.

3.3 Biosorption

Worldwide untreated wastewaters of different origins are released into lakes, rivers and oceans leading to long-term hazardous effect on flora and fauna of our ecosystem. These polluted waters are rich in inorganic pollutants such as heavy metals that pose dangerous risk to aquatic as well as human health. Apart from few heavy metals that are essential for our body, majority of other heavy metals are highly toxic in even scarce amount and have a tendency for bioaccumulation, and their toxicity level increases as they move up the food chain. Long-term consumption of water polluted with heavy metals has neurotoxic, carcinogenic and also mutagenic effects on human beings.

Heavy metals get exposed into environment by either natural or anthropogenic activities. Naturally corrosion of metals, eruption of volcanoes and soil leaching lead to heavy metals entering the ecosystem, while coal combustion in power plants and wastes from paint and textile industries come under anthropogenic causes.

Traditional methods that can be used to remove these toxic heavy metals from drinking as well as wastewaters are reverse osmosis, ultrafiltration, ion exchange, chemical precipitation and carbon adsorption (Wang and Chen 2009; Ahluwalia and Goyal 2007; Benaissa and Elouchdi 2007; Bunluesin et al. 2007).

Biosorption is described as the ability of certain biomaterials to take up heavy metals from drinking or wastewater via physiochemical or metabolically active pathways or by directly binding and adhering these heavy metal contaminants onto themselves when polluted waters with heavy metals are passed through them (Fourest and Roux 1992; Petersen et al. 2005; Volesky 2007). This biosorption process is efficient and cost-effective with low runtime and also safe for the environment.

3.3.1 Mechanism of Action

Various factors affect the mechanism of action of biosorption such as the material of the biomass and its types and properties and pollutants and their chemical composition along with concentration in the wastewater and also the environmental conditions in which the biomaterial is being used for biosorption (Petersen et al. 2005). The process of biosorption can be of two types: metabolism dependent and metabolism independent (Ahalya et al. 2003). Inside living cells when metal ions are absorbed after metabolism of food via cell wall or cell membrane, it is known as metabolism-dependent process, whereas when uptake of metal ions occurs via physical adsorption such as ion exchange or chemical sorption with the help of microbial biomass which are usually made up of polysaccharides along with protein and lipids, it is known as metabolism-independent process. These biomasses of microbial cell walls contain various functional groups such as aldehydic, ketonic, amide, carboxyl, sulphate, phosphate and amino groups that interact with the metal ions and thus help in their biosorption. Metabolism-independent processes are much faster when compared to metabolism-dependent processes and can also be reversible in nature (Kuyucak and Volesky 2008; Ercole et al. 1994). The parameter q_e is used to measure the amount of metal ions taken up or accumulated by per gram of biosorbent. The process of biosorption is affected by various parameters such as the pH and temperature of the metallic solutions, the concentration of the metal ions in the solution and also the nature and amount of biosorbent used (Kuyucak and Volesky 2008; Ercole et al. 1994; Asku et al. 1992; Galun et al. 1987; Fries and Keith 1986).

A biosorbent is considered good if it has high adsorption capacity along with being cheap, recovery of metal should be easy, and the recovered metal should be in reusable form. Biosorption is basically a passive process between a sorbent and a biological matrix (biosorbent). It is a metabolically independent process (Fomina and Gadd 2014). When biosorption is used in removing water pollutants, high biosorption efficiency which is the rate at which biosorbent can effectively remove water pollutants is taken into consideration. Biosorption is a process that depends on the physiochemical properties of the biosorbent, such as the molecular size and surface charge of the biosorbent and its solubility, reactivity and hydrophobicity, along with its chemical composition. Interactions such as aggregation, microprecipitation, oxidation and reduction, electrostatic interaction and ion exchange are those that commonly participate in this type of reaction (da Fontoura et al. 2017).

Surface sorption and interstitial sorption are the two types of interaction that take place between water pollutant and the biosorbent. In surface sorption process, the sorbent molecules (pollutants) move from the polluted wastewater to the surface of the biosorbent by passing through a boundary layer that surrounds the biosorbent, thereby attaching to the biosorbent's active sites. The interactions that mainly occur in these types of sorption processes are dipole-dipole, hydrogen bond and van Der Waals bonds (Sulyman et al. 2017). On the contrary, in interstitial sorption process, the sorbent molecules (pollutants) move via pores of the biosorbent and get biosorbed onto the inner surface of the biosorbent (Joseph et al. 2019) majorly by electrostatic interactions. Biosorption with interstitial sorption process is one of the major contributors towards removal of pollutants from wastewater because they have various functional groups that help them to bind and remove pollutants effectively. pH of the solution significantly affects the pollutant removal efficiency of the biosorbent; as with low pH, various functional groups get protonated, leading to the development of a net positive charge on the surface of the biosorbent. This leads to electrostatic repulsion and less sorption of positively charged pollutant molecules. However, when the pH of the solution is increased, it reduces the electrostatic repulsion between the pollutant and the biosorbent surface, thereby increasing biosorption of pollutants from wastewater by electrostatic attraction (Al-Wakeel et al. 2015). Ion exchange mechanism between the pollutant and the biosorbent also contributes in the biosorption process as the protons on the active sites on the surface of the biosorbent (having hydroxyl, carboxyl and phenol groups) get exchanged with the pollutants (metal ions) from the wastewater (Moreira et al. 2019). Here also the pH of the solution affects the efficiency of ion exchange because when low pH is maintained, increased H^+ concentration leads to competition between the positively charged pollutants and the functional groups of the biosorbent active site, whereas when high pH is maintained, increased OH^- concentration leads to competition between the negatively charged pollutants and the functional groups of the biosorbent active site.

3.3.2 Case Studies

Biosorption is a technique that has a dual benefit when applied to wastewater treatment as it is used to treat the waste material at minimum cost along with extracting maximum benefit from it (Gupta et al. 2019). Some of the studies that showed toxic dyes and heavy metals that can be extracted from heavily polluted wastewaters of various origins are (1) using chitosan studied by Almughamisi et al. (2020), (2) using biochar studied by Lei et al. (2019), (3) using activated carbon studied by Elwakeel et al. (2015), (4) using bio-nanocomposites studied by Jung et al. (2019), (5) using bio-hydrogels studied by Qi et al. (2019), (6) using macroalgae studied by Elgarahy et al. (2019a, b), (7) using agriculture wastes studied by Toumi et al. (2018) and (8) using bio-calcium carbonate studied by Arslanoğlu (2021).

Recent studies have established marine algae as one of the most effective sorbents for treating wastewater. These algae can be categorized as Chlorophyta, Phaeophyta and Rhodophyta and are generally found in oceans (Mokhtar et al. 2017). Afshariani and Schneider (Afshariani and Roosta 2019) have shown in their study that the sorption mechanism of methylene blue can be done by both batch and continuous processes in aqueous solution. When pH and temperature were maintained at 9 °C and 30 °C, respectively, the maximum sorption value was 87.69 ± 3.22 mg/g. In another experiment conducted by da Fontoura et al. (2017), biomass of defatted microalgae (waste of microalgae biofuel) was used. This biomass of defatted microalgae was examined as an alternative adsorbent of leather dye. The dye that was being biosorped was Acid Blue 161 aqueous dye solutions (AB-161). At temperature 25 °C, the maximum dye that was adsorbed was 75.78 mg/g, and at 40 °C, it was 83.2 mg/g. The result of the study concluded that 76.65% of dye was removed from the tannery waste effluents.

Algal cell walls are mostly composed of polysaccharides such as alginate, carrageenan and polycolloid, all of which have the capacity to remove various pollutants from wastewater (Daneshvar et al. 2017). da Rosa et al. (2018) showed that both micro- and macroalgae are useful for removing various heavy metals and organic dyes from water sources (Chen et al. 2019). A study conducted by Elgarahy et al. (2019a, b) revealed that green macroalgae (*Enteromorpha flexuosa*) can adsorb both the dyes crystal violet (CV) and methylene blue (MB) and the percentage removal of CV and MV was 90.3% and 93.4%, respectively, under optimum conditions.

Amin and Chetpattananondh (2019) studied biochar which is a derivative of microalgae pyrolysis for removing heavy metals from wastewater. Removal of Co (II) by this type of biochar has been studied in batch system with biosorption capacity of around 1.117 mg/g (Bordoloi et al. 2017). Another effective sorbent to remove heavy metals is biochar derived from water hyacinths (*Eichhornia crassipes*). As hyacinths are highly invasive species and have an impact on other aquatic life forms, thus biochar derived from hyacinths has an added benefit of reducing their impact on sensitive aquatic habitats. A study conducted by Liu et al. (2020) showed that capsules of biochar-alginates have the capacity to remove CD (II) in the range of 24.2–45.8 mg/g from aqueous solutions.

3.4 Bioaccumulation

Pollution by heavy metals is by far one of the most hazardous one because they are non-biodegradable and have a tendency to bioaccumulate in tissues and also get biomagnified as we move up the trophic level (Gray 2002). Once these heavy metals get released into the ecosystem, they start to accumulate in the food chain depending on their concentration and rate of uptake by local plants and animals. It has also been reported that in urban and sub-urban areas, these metals majorly get deposited by atmospheric deposition (Wuana and Okieimen 2011; Tchounwou et al. 2012).

Heavy metals can percolate into the ecosystem from various sources such as from tannery, dyeing, electroplating and mining industries, from agricultural lands, from sludge after treating solid sewage or from wastewater treatment plants. Many studies have already shown that industrial-untreated wastewater deteriorates water quality so much that it becomes unhealthy for human consumption (Wuana and Okieimen 2011). Chromium (Cr) and nickel (Ni) are one of those heavy metals that get discharged in untreated effluents of electroplating industries and are released in amount that surpasses the permissible limits (Srisuwan and Thongchai 2002; Sivasangari et al. 2016; Venkateswaran et al. 2007; Nriagu 1989; Orescanin et al. 2013). Tannery wastewater contains heavy metals such as copper (Cu), chromium (Cr), iron (Fe), manganese (Mn) and zinc (Zn) (Devi 2011).

In several parts of India, water contaminated with heavy metals above permissible limits is used for irrigation purpose leading to their bioaccumulation in the crops that are being cultivated and thus entering the food chains of various trophic levels. As industrialization is increasing so does the usage and release of heavy metals by industrial, domestic and agricultural sectors (Wuana and Okieimen 2011). The effect and intensity of adversity of these heavy metals depend on their chemical composition, for example, inorganic arsenic (As) is such a compound which promptly gets absorbed and thereby hinders cellular reactions, whereas organic forms are not so much harmful because of their low cellular absorption (Akter et al. 2005). Proteins have active binding sites where various metal ions bind for proper functioning of the protein molecules, but in the presence of heavy metals, the original metal ions are removed or blocked leading to cellular toxicity and malfunctioning (Jaishankar et al. 2014). To remove these heavy metals, different studies regarding bioremediation of these heavy metals using algae, bacteria and fungi have been studied.

Both processes be it biosorption or bioaccumulation require biological substance (biosorbent), a material on which the heavy metals get biosorbed, and an aqueous phase (water) which carries the contaminants that need to be removed. The major difference between biosorption and bioaccumulation is that being a passive process, biosorption makes use of dead biomass material for adsorbing the toxic metals onto their surfaces, whereas bioaccumulation is an active process, which utilizes living organisms for transporting and accumulating the heavy metals inside the cells (Chojnacka 2010; Timková et al. 2018). One major disadvantage of bioaccumulation is that when large amount of toxic metals gets bioaccumulated inside the cells, it leads to the death of the cells (Derco and Vrana 2018).

3.4.1 Mechanism of Action

As bioaccumulation is a metabolically active process, therefore, the living organisms that assimilate these heavy metals transport these metals from their intracellular space to the interior of the lipid bilayer. Once these heavy metals are inside the cells, they get sequestered by protein and peptide ligands (Malik 2004; Mishra and Malik 2013). The term "metabolically active" refers to the fact that bioaccumulation needs the host cell to be in living condition, and this poses a serious challenge as many heavy metals are detrimental to the growth of various microorganisms that are used for bioaccumulation.

There are some features that should be looked out for in bioaccumulation process when it comes to maximum efficiency of heavy metal removal by microorganisms. Metals such as cobalt, copper, manganese, iron and zinc (Yin et al. 2019) participate in cellular functioning and are therefore essential for survival of the microorganism, whereas metals such as mercury, cadmium and lead are highly detrimental for the growth and survival of microorganism (Filote et al. 2020; Rosca et al. 2015). As microorganisms grow through lag, log, stationary and declining phase, whenever the concentration of heavy metal to which the microorganism has been exposed is increased, the lag phase increases, and the index of maximum tolerance in the stationary phase decreases (Ge et al. 2011).

There are two important phases in bioaccumulation of heavy metals: first is the biosorption of these metals at the cell wall of the microorganism and second is the transfer of these metals from the cell wall to the intracellular structures via metabolic pathways and biotransformation.

Biosorption involves extracellular bond formation with the cell wall, and this happens rapidly, but the metabolic process of transfer of heavy metals inside intracellular structure is a slow process as the bond formation needs to occur between the metal ions and the intracellular proteins and ligands. Therefore, cell walls of specific chemical composition and functional groups are required in biosorption process and thus depend on the type of microorganism used (Hansda and Kumar 2016).

Biotransformation is a process that includes reduction, oxidation or alkylation which helps in creating metal ions with reduced toxic effects, whereas bioprecipitation is a process that helps in assembling metal ion chelates such as metallothioneins and phytochelatins (Hansda and Kumar 2016). The major forces that are involved in biosorption of metal ions are ion exchange, van der Waals forces and complexation. Other forces that are involved are metal reduction, proton release, biomethylation and chelation by ionic and covalent interaction (Leong and Chang 2020).

Microbial remediation process of wastewater with high amount of heavy metals includes the following: (1) bioaccumulation, (2) surface complexation, (3) bioprecipitation, (4) ion exchange, (5) electrostatic interactions and (6) cell surface adsorption (Ayangbenro and Babalola 2017; Hansda and Kumar 2016; Igiri et al. 2018).

3.4.2 Case Studies

Microbes that are naturally found in extreme conditions or even in contaminated sites have very high capacity of bioaccumulation. For example, in *Paecilomyces* fungi species, the minimum inhibitory concentration of cadmium was found to be 4000 mg/L (Fazli et al. 2015). In cyanobacterium *Microcystis aeruginosa* synthesis of chlorophyll deceased, when 20 mg Cd(II)/L, and 10–20 mg Pb(II)/L was found to bioaccumulate in their cells (Rzymski et al. 2014). Various studies have shown that chlorophyll synthesis gets hindered in presence of different zinc concentrations including species of *Chlorella* and *Scenedesmus* genera (Yang et al. 2015).

A study showed that fugal species such as *Trichoderma* has a high tolerance towards cadmium, withstanding concentration up to 1000 mg/L (Fazli et al. 2015). In another study conducted on species of filamentous fungi that were isolated from Malaysian river sediments, out of the 41 species that were collected to experiment whether these specimens can survive a concentration of 5000 mg/L of Pb(II), only *Aspergillus niger* as a species survived. In this same study, *Penicillium simplicissimum* species survived and tolerated concentration of Cu(II) up to 1000 mg/L (Iskandar et al. 2011). Another study compared tolerance of *Aspergillus niger* with *Penicillium chrysogenum* and showed that the later has a higher tolerance to chromium concentration of up to 800 μg/mL (Jayanthi et al. 2014).

Rhamnolipid is a biosurfactant, which helps in metal complexation, so along with microbes, these biosurfactants are used for remediation of metal ions (Chellaiah 2018).

The most frequent form of naturally occurring chromium is hexavalent Cr (VI) and trivalent Cr(III). Cr(III) is essential for proper cellular functioning, but Cr (VI) turns out to be much more soluble, mobile and toxic than Cr(III) (Biedermann and Landolph 1990). Studies have shown that bacteria such as streptomycetes have the capability to reduce Cr(VI) (Laxman and More 2002).

Minimal medium (MM) and minimal glycerol medium (MMY) were used by Polti et al. to grow *Streptomyces* MC1 strain in addition to 50 mg/L of Cr(VI). This study concluded that, when glycerol was used, 96% of Cr(VI) was reduced to Cr(III) by *Streptomyces* MC1 strain and 8% of Cr(III) was bioaccumulated by the strain after 70 days of incubation in MMY. This same study showed that when this strain was incubated for 7 days in MM and MMY, the specific uptake of Cr(III) was 1.48 mg/g and 1.56 mg/g wet biomass, respectively, and this uptake increased to 3.54 mg/g and 2.32 mg/g wet biomass, respectively, after 70 days (Polti et al. 2011).

3.5 Biodegradation

Since industrialization, petroleum and petroleum-based products have become part of our day-to-day lives, but what we tend to overlook are the accidental spills and leaks that happen when these products are extracted, manufactured, refined, transported and stored. It has been estimated that there is a seepage of almost 600,000 metric tons of natural crude oil per year (Kvenvolden and Cooper 2003). One of the major causes of water and soil pollution is the release of these hydrocarbon products either accidentally or deliberately by humans (Holliger et al. 1997). Bioaccumulation of these petroleum-based products in plant and animal due to these types of products being released in soil and water leads to hazardous health effects (Alvarez and Vogel 1991).

One of the bioremediation processes that can effectively remove and degrade these petroleum and petroleum-based products is biodegradation. Biodegradation is much more efficient and also cost-effective when compared to conventional methods of soil remediation such as mechanical, burying, evaporation, dispersion and washing (Ulrici 2000; Leahy and Colwell 1990).

Studies have shown that the success rate of oil biodegradation in the contaminated sites depends on few factors that need to be applied and maintained (Leahy and Colwell 1990; Zobell 1946; Atlas 1981, 1984; Atlas and Bartha 1992; Foght and Westlake 1987). One of these factors that enhances oil biodegradation is utilizing microbes with adequate nutrient availability and maintaining proper growth conditions such as pH between 6 and 9. This type of bioremediation process is also determined by the nature of the oil and oil-contaminated areas such as their physical and chemical compositions.

The two main methods that are applied to oil spill bioremediation are (a) bioaugmentation process: potential oil-degrading bacteria that are applied to the oil-contaminated site to help the indigenous microbial population to degrade the oil better and (b) biostimulation: the growth of native oil-degrading microbial population that is enhanced by adding nutrients and other substrates.

3.5.1 Mechanism of Action

The most effective way by which almost all of the petroleum-based organic pollutants are degraded is usually under aerobic circumstances. Fig. 3.1 depicts the fundamental by which hydrocarbons are degraded aerobically (Fritsche and Hofrichter 2000). The first step in this reaction is an oxidative process, and the activation of oxygen as well as its incorporation is carried out by oxygenases and peroxidases. Pathways that follow peripheral degradation method break down organic pollutants in a step-by-step manner into intermediates that contribute to some central metabolic pathways such as tricarboxylic acid (TCA) cycle, and the precursor metabolites of these central metabolic pathways such as acetyl-CoA, succinate and pyruvate contribute towards the synthesis of cell biomass. Carbohydrates which are vital for cell growth are biosynthesized via gluconeogenesis.

Generation of biosurfactants and attachment of microbes to their specified substrates (oil droplets) are methods other than discrete enzyme system which can degrade petroleum-based hydrocarbons (Hommel 1990). Cytochrome P450 alkane hydroxylase is one such enzyme which has a massive role in microbial degradation of petroleum-based oils and hydrocarbons, additives of fuels and other such compounds (Van Beilen and Funhoff 2007). To start biodegradation, hydrocarbon

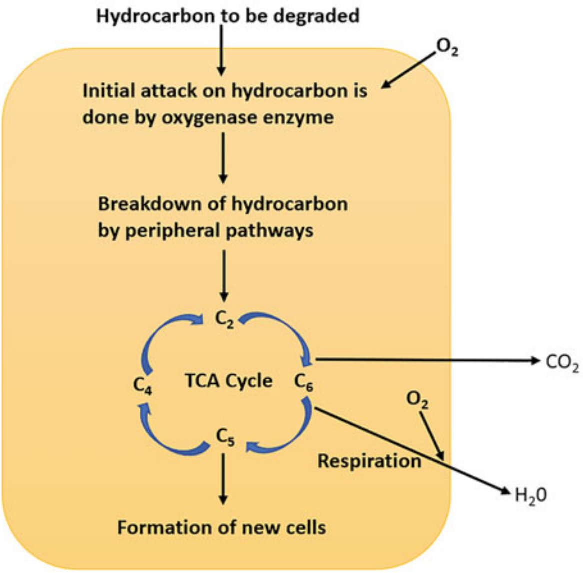

Fig. 3.1 Aerobic degradation pathway of hydrocarbons by microorganism

chain length is a critical factor as based on that, the enzyme required for degradation needs to be determined. Several different isomeric forms of this enzyme are found in higher eukaryotes, which generally work together in the pathway for biodegradation of petroleum-based hydrocarbons, but in microbial family, this type of enzyme is only synthesized in few species (Zimmer et al. 1996). However, certain yeast species such as *Candida maltosa*, *Candida tropicalis* and *Candida apicola* (Scheuer et al. 1998) have different isomeric forms of microsomal cytochrome P450 which enable them to break down hydrocarbons such as *n*-alkanes and other aliphatic ones and use them directly as sole source of carbon and energy.

Certain microorganisms produce active chemical compounds known as biosurfactants which have the capability of enhancing the solubilization mechanism of these hydrocarbons by increasing the bioavailability of these compounds (Muthusamy et al. 2008; Mahmound et al. 2008; Ilori et al. 2005, 2008; Kiran et al. 2009; Obayori et al. 2009; Brusseau et al. 1995; Bai et al. 1997; Barkay et al. 1999). They help to break down these oil droplets into smaller particles by acting as emulsifying agents, thereby decreasing the surface tension between the molecules and forming micelles. They also increase the surface area of the oil particles for their maximum availability towards the bacteria, so that the bacteria can degrade them much easily (Nikolopoulou and Kalogerakis 2009).

3.5.2 Case Study

A study was conducted by Cameotra and Singh (2008) on oil sludge biodegradation by using biosurfactants. This study utilized a consortium of microbes having two isolated strains of *Pseudomonas aeruginosa* and one isolated strain of *Rhodococcus erythropolis* procured from oil sludge-contaminated soil. When this consortium was grown in liquid culture media, they were responsible for 90% of hydrocarbon degradation. Two individual field trials were conducted to verify the effectiveness of this microbial consortium to degrade hydrocarbon from sludge. Apart from this, two additives, one a nutrient mixture and another a crude biosurfactant, were tested for their efficiency. The species of the microbial consortium which produced the biosurfactant was recognized as being a combination of 11 rhamnolipid congeners. This consortium was able to break down 91% of the hydrocarbons in 5 weeks, from the soil sample polluted with 1% (v/v) crude oil sludge. With the consortium when only one additive was tested, the result was breakdown of about 91–95% of the hydrocarbons in about 4 weeks' time, and it was also shown that as an enhancer, the preparation made from crude biosurfactant was much more effective in biodegradation. But, when along with the consortium both the additives were added, then higher than 98% of the hydrocarbons were broken down. This study affirmed the potential of crude biosurfactant in the process of oil sludge hydrocarbon degradation.

3.6 The Choice of Sustainable Approaches of Environmental Contaminants

From previous sections, we now know that biomass is the major component in the process of biosorption, and in a broader sense, the term biomass includes living as well as dead and their derived biological components such as wastes, charcoal, etc. The major application of this technique is heavy metal removal and even recovery in some cases, from contaminated industrial wastewaters. As this technique is very efficient in removing heavy metal pollutants, as well as is cost-effective and environmental friendly, various methods have been assessed to increase the sorption capabilities.

When it comes to bioaccumulation, this process only utilizes living organism for uptake of toxic metal pollutants and actively transports these metals inside their cells where they get accumulated for further degradation by several metabolic pathways. So, biosorption and bioaccumulation are both majorly used for removal of heavy metal pollutants, but the choice between these two techniques depends on conditions such as temperature, pH of polluted soil and water and types of microbes. The surface composition of the microbes also affects the degradation process, because metals can alter the charges on the surface of the microbes. The polluted soil and water support the growth of the preferred culture of microbes used for bioaccumulation, which tend to get inhibited by low nutrient conditions, inadequate temperature, and metal toxicity. When it comes to metal recovery process, biosorption is a better choice over bioaccumulation as in the latter process, the metal gets biotransformed due to the metabolic activity of the microbes which is not the case with biosorption. Thus, the metals can be easily recovered as biosorption uses dead biomass and the process is reversible (Timková et al. 2018).

The process of microbial degradation is required when there is a need to degrade and remove petroleum hydrocarbon pollutants from contaminated soil areas. Petroleum hydrocarbons have four major classes, the saturates, the aromatics, the asphaltenes (phenols, fatty acids, ketones, esters and porphyrins) and the resins (pyridines, quinolines, carbazoles, sulfoxides and amides) (Colwell et al. 1977), and depending on these classes, the microbial consortium that can degrade them should be chosen. One main factor that needs to be followed when choosing the microbial population is that these oil contaminants have limited availability towards the microbes and therefore they are difficult to be degraded and removed, so only such microbial consortium should be chosen that have the capability to degrade them (Barathi and Vasudevan 2001).

3.7 Conclusion and Future Prospects

Biosorption is one of the green approaches used for removing heavy metal from industrial wastewater. Various physical and chemical treatments such as sonication and freeze-drying as well as techniques that can alter the porosity and surface area of the sorption biomass are being currently studied which can thereby increase the availability of sorption sites by increasing the number of binding sites on the surface of the biosorbent. Though there had been a significant growth in the development of various biosorbents, there are various challenges linked with these materials that need further research such as stability of these materials in various pH conditions, their capacity of sorption, textural properties and durability, etc. Various studies have indicated that composite beads made up of chitosan and alginate have the potential to effectively bio-absorb pharmaceuticals as well as other organic and inorganic pollutants from wastewater making them an area of future research.

Bioaccumulation is another green technology that is capable of removing heavy metals from wastewater as well as from polluted soil areas. And for doing this, the microorganisms used should be chosen based on their capability to tolerate and remove these metals efficiently, and all of this depends on the intra- and extracellular complex metabolic pathways of the microorganisms. The various mechanisms that are majorly used by these microorganisms to remove these heavy metals include biosorption, bioaccumulation, biotransformation, bioprecipitation, reduction of metals and chelation by ionic and covalent interaction. Further studies should focus on commercial scaling up of biosorption and bioaccumulation processes for polluted soil and water body clean-up.

Biodegradation of petroleum hydrocarbons can be effectively done with indigenous microbial population by the process of bioaugmentation and biostimulation. Several recent studies have shown that the use of genetically modified microorganisms (GEMs) can better degrade these types of pollutants better than indigenous ones. But, ecological and environmental concerns along with tight regulatory practices have not allowed the uses of these GMOs on polluted sites, which if solved can make these GEMs to become a much more efficient clean-up process that too at a lower cost.

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4

Bioremediation Technologies for the Treatment of Water Contaminated by Organic and Inorganic Contaminants

Huma Ilyas, Joyabrata Mal, Ilyas Masih, and Eric D. van Hullebusch

Abstract

This chapter explains the significance of the removal of selected categories of organic contaminants (polycyclic aromatic hydrocarbons, petroleum hydrocarbons, azo dyes, chlorinated solvents, pharmaceuticals, personal care products, steroidal hormones, and pesticides) and inorganic contaminants (nutrients, metal(loid)s, and radioactive compounds) from the wastewater while synthesizing the available knowledge on the sources of these types of contaminants in water resources and the environment as well as the societal challenges related to their discharge. The available wastewater treatment technologies (physicochemical and bioremediation techniques) for these types of contaminants are described in this chapter with the detail description of bioremediation techniques (microbial remediation (microbes (e.g., bacteria)), mycoremediation (fungi), phycoremediation (algae), and phytoremediation (plants)). The concept of constructed wetlands, which is a phytoremediation technique, is discussed for the treatment of wastewater containing the selected

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categories of organic and inorganic contaminants. Finally, the main findings, key insights, and specific conclusions are summarized.

Keywords

Bioremediation · Biodegradation · Organic contaminants · Inorganic contaminants · Constructed wetland

4.1 Introduction

Freshwater, which is essential in all environmental life cycles, is a finite resource. The natural quality of water that is mainly determined by the geology and hydrology of a river or lake basin can be deteriorated by a wide range of pollutants and processes (e.g., chemical weathering, volcanic fallout, plant decay, atmospheric inputs, aeolian erosion, recycled oceanic aerosols, leaching of organic soils, and primary production and respiration) (Chapman 1996; Field and Sierra-Alvarez 2004; Abdel-Shafy and Mansour 2016; Li et al. 2017a; Cui et al. 2018; Tanmoy and Saha 2019). In addition to natural sources, the organic and inorganic pollutants are discharged to water resources and the environment through various anthropogenic sources. The organic contaminants are classified as priority substances (pose a significant risk to and via the aquatic environment) or emerging organic contaminants (EOCs) depending upon the existence or absence of regulation, respectively (USEPA (United States Environmental Protection Agency) 1977; EU (European Union) 2013, 2015, 2018; Barbosa et al. 2016; Sun et al. 2016; Gorito et al. 2017; Loos et al. 2018). The major sources of organic pollutants (polycyclic aromatic hydrocarbons (PAHs), petroleum hydrocarbons, azo dyes, chlorinated solvents, pharmaceuticals (PhCs), personal care products (PCPs), steroidal hormones (SHs), and pesticides) into water resources and the environment are summarized in Table 4.1.

Furthermore, conventional wastewater treatment plants (WWTPs) are not specifically designed for the treatment of organic contaminants (e.g., Luo et al. 2014; Gorito et al. 2017). Therefore, WWTPs are also one of the major sources of these organic contaminants into water resources and the environment. Although these organic contaminants are found to be in relatively small concentrations (e.g., ng/L to μg/L) in water resources, their presence (as individual compounds, transformation products (TPs), and multitude of compounds) could pose risk to aquatic and terrestrial life (Barbosa et al. 2016; Gorito et al. 2017; Vystavna et al. 2017; Tran et al. 2018). It has been indicated that higher concentration of EOCs compared with their potential no-effect concentration could pose severe risk to human health, since many of these EOCs are considered as prospective endocrine disruptors (EDCs) (Caliman and Gavrilescu 2009; Vymazal et al. 2015; Gogoi et al. 2018). EDCs are characterized as external agents that obstruct the formation, release, transport, attachment, activity, or displacement of body's natural hormones that regulate homeostasis, development, reproduction, and behavior (USEPA 1997; Vogel

Table 4.1 Sources of organic and inorganic contaminants into water resources and the environment

Categories of contaminants	Compounds/classes	Major sources in water resources and environment	References for major sources
Organic contaminants			
Polycyclic aromatic hydrocarbons	Naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo (a)pyrene, benz (a)anthracene, benzo (b)fluoranthene, benzo (k)fluoranthene, dibenz (a,h)anthracene, indeno (1,2,3-c,d)pyrene, benzo(g,h,i)perylene	• Urban wastewater (from car traffic, waste incinerators, and domestic heating via both atmospheric transport and local activity)	Fontoulakis et al. (2009), Abdel-Shafy and Mansour (2016), Noman et al. (2019)
		• Industrial wastewater (from product manufacturing discharges)	
		• Landfill leachate (from improper disposal of used, defective, or expired items)	
Petroleum hydrocarbons	*BTEX*: benzene, toluene, ethylbenzene, xylene	• Oil spills from underground storage tanks, pipelines, and land vehicles	Garoma et al. (2008), Hewelke et al. (2018), Xu et al. (2018), Abdullah et al. (2020), Mohammadi et al. (2020)
		• Accidental spills during transportation	
		• Industrial wastewater	
		• Drilling sites	
		• Landfill leachate	
Azo dyes	*Monoazo*: yellow reactive 4, acid yellow 23, acid red 14, food red 17	• Domestic wastewater (food additives, hair colorants)	Grčić et al. (2015), Hasanbeigi and Price (2015), Sarkar et al. (2017), Berradi et al. (2019), Noman et al. (2019), Benkhaya et al. (2020), Ali et al. (2021), Saloglu and Sahin (2021)
	Diazo: black reactive 5, direct red 28	• Industrial wastewater (textile, leather, food and paper processing, pharmaceuticals, cosmetics)	
	Triazo: direct blue 71, direct black 28	• Landfill leachate	
	Polyazo: direct red 80, direct black 32, direct black 28, direct black 22		
Chlorinated solvents	*Chlorinated methanes*: chloromethane, dichloromethane,	• Domestic wastewater (leaching from PVC pipes)	Wilkie et al. (1996), USEPA (2009), Field and Sierra-Alvarez (2004), Rule et al.

(continued)

Table 4.1 (continued)

Categories of contaminants	Compounds/classes	Major sources in water resources and environment	References for major sources
	trichloromethane, tetrachloromethane		(2006), Chen et al. (2017a)
	Chlorinated ethanes: 1,1,1-trichloroethane, hexachloroethane, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane	• Industrial wastewater (discharge from drug, chemical, and plastic factories)	
	Chlorinated ethenes: chloroethene, 1,1-dichloroethylene, trichloroethylene, tetrachloroethylene	• Landfill leachate	
Pharmaceuticals	Analgesic/anti-inflammatory drugs, antibiotics, lipid regulators, beta-blockers, stimulants/psychoactive drugs, antidiabetics, psychiatric drugs, diuretics	• Domestic wastewater (from excretion) • Hospital effluents • Runoff from concentrated animal feeding operations and aquaculture • Industrial wastewater • Landfill leachate	Luo et al. (2014), Barbosa et al. (2016), Gorito et al. (2017)
Personal care products	Preservatives, artificial sweeteners, insect repellents, antiseptics, fragrances, sunscreen agents, flame retardants	• Domestic wastewater (from bathing, shaving, spraying, swimming, etc.) • Industrial wastewater • Landfill leachate	Töre et al. (2012), Luo et al. (2014), Barbosa et al. (2016), Tran et al. (2019)
Steroidal hormones	Estrogens, androgens, progestogens, glucocorticoids	• Domestic wastewater (from excretion) • Runoff from concentrated animal feeding operations and aquaculture • Industrial wastewater • Landfill leachate	Luo et al. (2014), Ribeiro et al. (2015), Barbosa et al. (2016), Gorito et al. (2017), Gogoi et al. (2018)
Pesticides	Insecticides, herbicides, fungicides	• Domestic wastewater (from improper cleaning; runoff from gardens, lawns, and roadways; etc.) • Agricultural runoff • Industrial wastewater • Landfill leachate	Moore et al. (2002), Slack et al. (2005), Luo et al. (2014), Vymazal and Březinová (2015), Lv et al. (2016), Lyu et al. (2018)

(continued)

Table 4.1 (continued)

Categories of contaminants	Compounds/classes	Major sources in water resources and environment	References for major sources
Inorganic contaminants			
Metal(loid)s	Potentially toxic metal (loid)s as micronutrients: manganese, copper, zinc, cobalt, selenium	• Mining	Choudhary et al. (2017), Tanmoy and Saha (2019), Hirvaniya et al. (2021)
	Toxic metal(loid)s: cadmium, chromium, lead, arsenic, selenium, mercury	• Extraction or refining ores	
		• Agricultural drainage due to use of pesticides and chemical fertilizers	
		• Industrial wastewater	
		• Coal-based thermal power plants	
Radionuclides	Uranium-238 (^{238}U), ^{235}U, radon-222 (^{222}Rn), technetium-99 (^{99}Tc), plutonium-239 (^{239}Pu), thorium-232 (^{232}Th), cobalt-60 (^{60}Co), radium-226 (^{226}Ra), iridium-192 (^{192}Ir), thallium-201 (^{201}Tl), strontium-90 (^{90}Sr), cesium-137 (^{137}Cs)	• Uranium mining and milling	Das (2012), Prakash et al. (2013), Francis and Nancharaiah (2015), Shukla et al. (2017)
		• Nuclear fuel reactor facilities and operation of nuclear power plants	
		• Testing nuclear power weapons	
		• Disposal of nuclear wastes	
		• Drilling and production of oil and gas	
		• Coal combustion	
		• Phosphate mining and extraction of rare-earth elements	
		• Fatal nuclear power plant accidents	
		• Broad application of radioactive materials at various research including biomedical and industrial application	

2005; Ra et al. 2010). Moreover, the continuous discharge of organic contaminants through various sources including WWTPs could make these “pseudo-persistent” organic chemicals a potential source of risk, especially when present in high concentrations, and the combination of a wide range of compounds may act synergistically (e.g., Gorito et al. 2017).

Table 4.2 Major metal(loid)s and radionuclides and their toxic effects

Metal(loid)	Toxicity	Maximum concentration limit in discharged wastewater (mg/L)
Cadmium (Cd)	Lung cancer and kidney damage, central nervous system abnormalities, aborted fetus	0.005
Chromium (Cr)	Carcinogenic, dermatological damage, nosebleed, ulcer, damaging immune system, genetic material alteration, liver and kidney damage	0.1
Copper (Cu)	Wilson disease, liver and kidney damage, anemia, disrupt nutrition cycle, stomach and intestinal irritation	1.3
Iron (Fe)	Cancer, hemochromatosis, eye disorder, and heart diseases	0.3
Nickel (Ni)	Carcinogenic, cell death and chromosomal abnormality, skin dermatitis, and renal edema	0.2
Lead (Pb)	Lung and kidney damage, central nervous system dysfunction	0.015
Zinc (Zn)	Pancreatic damage and protein metabolism disruption, respiratory disorders	0.8
Mercury (Hg)	Mutagenic and teratogenic, lung and kidney damage, eye problems, skin dermatitis, central nervous system dysfunction	0.002
Arsenic (As)	Arsenicosis, cancers of the bladder, lungs, kidneys, and skin	0.01
Selenium (Se)	Nail and hair loss, skin lesions, nausea, diarrhea, fatigue, irritability, and nervous system abnormalities, teratogenic	0.05
Uranium (U)	Carcinogenic, bone and liver cancer, kidney damage	0.03

Note: Data are taken from Choudhary et al. (2017) and Hirvaniya et al. (2021)

Among the inorganic contaminants are nutrients, metal(loid)s, and radioactive compounds. The major sources of these inorganic contaminants into water resources and the environment are summarized in Table 4.1. Pollution due to industrial discharge of potentially toxic metals (PTMs) to the environment is a serious threat due to the toxic effect of PTMs on the environment and human health. PTMs being nonbiodegradable and having the tendency to bioaccumulate via food chain and biomagnify along the trophic levels makes it a serious concern for living organisms even at small concentration (Mal and Rangabhashiyam 2021; Yin et al. 2019). PTMs' contamination, accumulation, and toxicity in plants and animals have been explored extensively (Singh and Kalamdhad 2011; Tchounwou et al. 2012). While some PTMs (e.g., zinc (Zn), copper (Cu), iron (Fe), nickel (Ni)) are essential micronutrients, all can be harmful after certain level, i.e., beyond permissible limit. Hence, the standard permissible limit for the environmental discharge of PTMs has been set by USEPA and the World Health Organization (WHO) (Table 4.2).

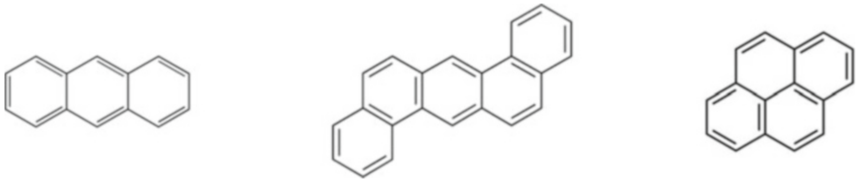
The main objective of this chapter is to discuss the occurrence of organic and inorganic contaminants in the wastewater and their removal by bioremediation techniques. The specific objectives are (1) to explore the sources of organic and inorganic contaminants in water resources and environment; (2) to investigate the environmental risk posed by the organic and inorganic contaminants; (3) to synthesize the available knowledge on the removal of organic and inorganic contaminants by different types of bioremediation methods; and (4) to summarize the available evidence on major removal mechanisms of organic and inorganic contaminants by different types of bioremediation methods.

The following sections describe the types, sources, and environmental risks of selected categories of organic contaminants (PAHs, petroleum hydrocarbons, azo dyes, chlorinated solvents, PhCs, PCPs, SHs, and pesticides) and inorganic contaminants (metal(loid)s and radioactive compounds) in water resources and the environment, biotechnology applications for the removal of these contaminants from the wastewater, and conclusions. The section of types, sources, and environmental risks of contaminants presents the available knowledge on the types and sources of these contaminants in water resources and the environment as well as the societal challenges related to their discharge. The section of biotechnology applications describes the available biological wastewater treatment technologies (bioremediation techniques: microbial remediation (microbes (e.g., bacteria)), mycoremediation (fungi), phycoremediation (algae), and phytoremediation (plants)) for the treatment of wastewater containing these types of contaminants. The concept of constructed wetlands, which is a phytoremediation technique, is discussed in detail for the treatment of wastewater containing the selected categories of organic and inorganic contaminants. Finally, the key insights and conclusions are summarized in the conclusion section.

4.2 Description of Organic Contaminants

4.2.1 Polycyclic Aromatic Hydrocarbons

The PAHs are discharged to water resources and environment through various sources such as urban and industrial wastewater and landfill leachate (Table 4.1). USEPA (1977) classified 16 compounds of PAHs as toxic and priority pollutants (Table 4.1), which occur in the aquatic environment (Sun et al. 2016). PAHs (composed of carbon and hydrogen) are chemically comprised of multiple benzene rings bonded in linear, angular, or cluster arrangements (Fig. 4.1) (Di-Toro et al. 2000; Arey and Atkinson 2003). PAHs have two or more single or fused aromatic rings (a pair of carbon atoms shared between rings) and are classified as small and large PAHs comprised of six and more fused aromatic rings, respectively (Abdel-Shafy and Mansour 2016). The major routes of exposure to PAHs can be inhalation of air, ingestion of water and food contaminated with PAHs, or direct dermal contact (Suess 1976), for instance, inhalation of tobacco smoke which contains a variety of PAHs (e.g., benzo(a)pyrene) and more than 40 potential and probable human

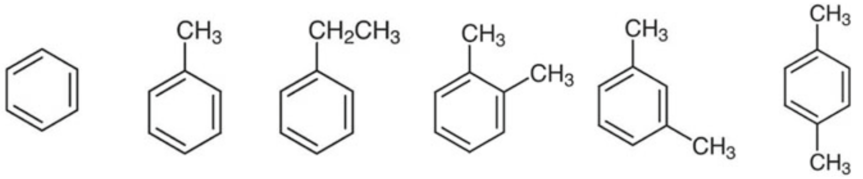


Linear: e.g., anthracene ($C_{14}H_{10}$)

Angular: e.g., Dibenz (a,h) anthracene ($C_{22}H_{14}$)

Cluster: e.g., Pyrene ($C_{16}H_{10}$)

Fig. 4.1 Molecular arrangements of polycyclic aromatic hydrocarbons (PAHs). Note: Molecular formula and structure are taken from the websites: https://www.ncbi.nlm.nih.gov/pccompound and https://images.google.com/



Benzene (C_6H_6)

Toluene (C_7H_8)

Ethylbenzene (C_8H_{10})

Ortho-xylene (C_8H_{10})

Meta-xylene (C_8H_{10})

Para-xylene (C_8H_{10})

Fig. 4.2 Molecular formula and structure of petrochemical hydrocarbon pollutants (BTEX). Note: Molecular formula and structure are taken from the websites: https://www.ncbi.nlm.nih.gov/pccompound and https://images.google.com/

carcinogens (Lannerö et al. 2008). The aromatic hydrocarbons are destructive to the central nervous system and can cause bone marrow suppression and musculoskeletal malformations (Singh et al. 1992). In addition to that, the occurrence of PAHs in the aquatic ecosystem may pose risks to microorganisms and other aquatic organisms as well as to humans, since they are not only cytotoxic but also mutagenic and carcinogenic (Moubasher et al. 2015; Abdel-Shafy and Mansour 2016). The detailed description about the physicochemical properties and carcinogen classification of PAHs can be found in the literature (e.g., USEPA 1977; Khalid et al. 2021).

4.2.2 Petroleum Hydrocarbons

Petroleum hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX) are among the natural compounds of crude oil and petrol, which are found in surface and groundwater (Mohammadi et al. 2020; Stefanakis 2020). The substitution of methyl or ethyl with the hydrogen atoms in the benzene ring results in new compounds such as toluene (methylbenzene), xylene (dimethyl benzene), and ethylbenzene. Xylene exists as three different isomers: *ortho*-, *meta*-, and *para*-xylene (Shim et al. 2002) (Fig. 4.2). Among the sources of these compounds to water resources and the environment are industrial wastewater, accidental spills during transportation, reservoir leakage, and landfill leachate (Table 4.1). Diesel oil, a complex petroleum hydrocarbon obtained during the distillation of crude oil, is made up of low molecular weight alkanes and PAHs (5–30%) (Kaur et al. 2015). Ramadass et al. (2017) assessed the toxicity of diesel and its water accommodated fraction toward two microalgal species, *Pseudokirchneriella subcapitata* and *Chlorella* sp. MM3. The authors reported the occurrence of main toxic compounds from diesel water accommodated fraction above the limits of safe concentration level for the aquatic environment, including BTEX. BTEX are listed among the harmful and important toxins that must be eliminated from industrial effluents before their release to the environment (USEPA 1977). The aromatic hydrocarbons are destructive to the central nervous system and can cause bone marrow suppression and musculoskeletal malformations (Singh et al. 1992). Petrochemical hydrocarbons, including BTEX, are indicator for exposure to volatile organic and petroleum compounds (Schneider et al. 1999). The contact with BTEX can occur through inhalation of water and air contaminated with BTEX or adsorption through the skin (Sairat et al. 2015). Their presence in the environment can pose risks because these are carcinogenic (benzene), can damage the ozone layer (toluene), can produce photochemical smog and pose mutagenic hazards (ethylbenzene), and can cause neurological disorders, and kidney, liver and skin problems (xylene) (Mohammadi et al. 2020). Although BTEX vaporize when these are exposed to the environment, some compounds dissolve in water (Mohammadi et al. 2020). The maximum allowable concentration of benzene, toluene, ethylbenzene, and xylene in drinking water is 10 μg/L, 700 μg/L, 300 μg/L, and 500 μg/L, respectively, based on the WHO standard (Mohammadi et al. 2020). The water solubility of benzene, toluene, ethylbenzene, and xylene is 1780, 535, 152, and 175 mg/L. The detailed description about the other physicochemical properties and carcinogen classification of petroleum hydrocarbons can be found in the literature (e.g., USEPA 1977; Jain et al. 2020; Mohammadi et al. 2020; Stefanakis 2020; Khalid et al. 2021).

4.2.3 Azo Dyes

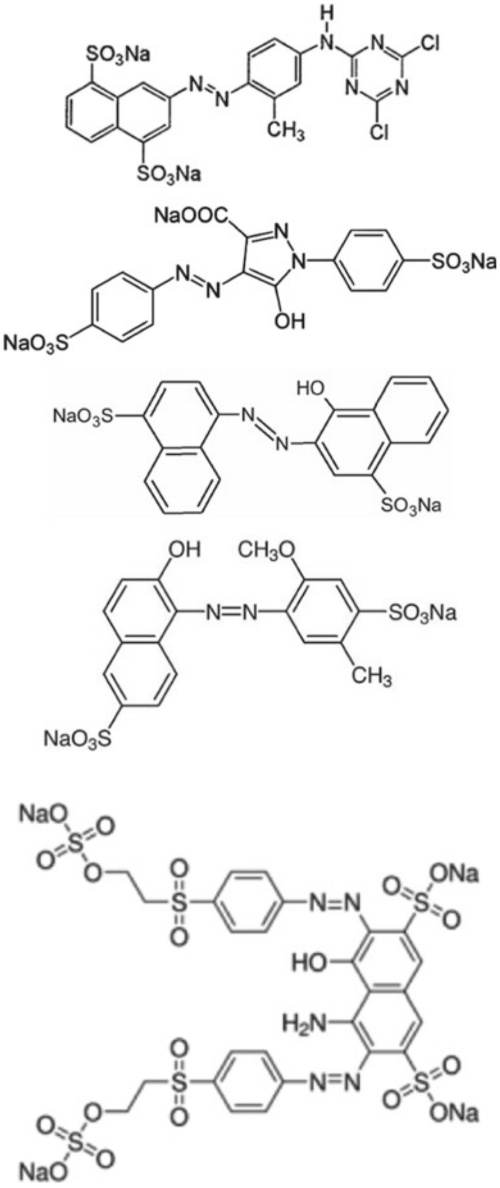
Azo dyes are discharged to water resources and environment through various sources such as domestic and industrial wastewater, landfill leachate, and effluent discharge from WWTPs (Table 4.1). Azo dyes are the most used dyes that account for more than 60% of the total dyes (Fu and Viraraghavan 2001; Shah 2014; Gürses et al. 2016; Overdahl et al. 2021) and about 70% of all the dyes used in industry (Lim et al. 2010; Rajasimman et al. 2017; Lipskikh et al. 2018; Berradi et al. 2019; Khan et al. 2020; Overdahl et al. 2021). Among the commonly used azo dyes are benzidine-based azo dyes (e.g., direct black 38), direct black 32, direct black 28, direct black 22, direct blue 15, direct blue 71, acid violet 7, malachite green (basic green 4), black reactive 5, disperse red 1, disperse red 13, Congo red (direct red 28), sirius red (direct red 80), allura red (food red 17), carmoisine (acid red 14), acid orange 7, yellow reactive 4, tartrazine (acid yellow 23), and amaranth (acid red 27) (e.g., Manning et al. 1985; Amin et al. 2010; Sarkar et al. 2017; Rawat et al.

2018; Saloglu and Sahin 2021). The azo dyes are characterized by the presence of azo group (–N=N–) linking two symmetrical and/or asymmetrical identical or non-azo alkyl or aryl radicals (Benkhaya et al. 2020). The azo dyes can be classified as monoazo, diazo, triazo, and polyazo depending upon the number of azo group (one, two, three, or more) linked to the auxochrome groups including hydroxyl, sulfo, or amino groups (Holkar et al. 2016; Saini 2017; Berradi et al. 2019; Collivignarelli et al. 2019) (Fig. 4.3). The azo dyes are resistant to biodegradation, photodegradation, ozonation, and oxidation (Yagub et al. 2014; Saloglu and Sahin 2021). The detailed classification of azo dyes based on number of azo groups and according to reactive functional groups can be found in the literature (e.g., Berradi et al. 2019; Benkhaya et al. 2020).

Several studies have indicated that the occurrence of azo dyes in the water resources has negative impacts on aquatic environments and human. In addition to the aesthetic problems (color and odor), these can cause health problems in humans such as allergies, skin irritations, and dermatitis as well as these show mutagenic, carcinogenic, genotoxic, and teratogenic effects (e.g., Brüschweiler and Merlot 2017; Liang et al. 2017; Rawat et al. 2018; Sarvajith et al. 2018; Berradi et al. 2019). For instance, benzidine-based azo dyes are carcinogenic to human (e.g., bladder cancer) and tumorigenic to laboratory animals (Manning et al. 1985), and tartrazine provokes asthma attacks in children, produces hyperactivity syndrome and thyroid tumors by combining with benzoates, and causes agitation, confusion, rhinitis, migraine, and infertility (Balta et al. 2019). Carmoisine produces carcinogenicity and biochemical toxicity in mice (Reza et al. 2019; Khan et al. 2020). Allura red causes toxicity and carcinogenicity (e.g., bladder cancer) (Gičević et al. 2020). The excess dose of tartrazine presents effects on peripheral nerves, paraesthesia, and dental changes (Balta et al. 2019), carmoisine damages the liver and decreases the function of some main metabolic enzymes (Amin et al. 2010; Khan et al. 2020), and allura red reduces intestinal anaerobic bacteria (Gičević et al. 2020). The Food and Agriculture Organization (FAO)/WHO established an acceptable daily intake for tartrazine, carmoisine, and allura red of 7.5 mg/kg b.w./day, 4.0 mg/kg b.w./day, and 7.0 mg/kg b.w./day, respectively (EFSA (European Food Safety Authority) 2009a, b, c; Balta et al. 2019; Gičević et al. 2020; Khan et al. 2020). The detailed discussion on the environmental risk of azo dyes in the wastewater and their physicochemical properties can be found in the literature (e.g., Brüschweiler and Merlot 2017; Sarkar et al. 2017; Rawat et al. 2018; Balta et al. 2019; Gičević et al. 2020; Khan et al. 2020; Overdahl et al. 2021).

4.2.4 Chlorinated Solvents

Chlorinated solvents are discharged to water resources and environment through various sources such as domestic and industrial wastewater and landfill leachate (Table 4.1). There are several types of chlorinated solvents, which are grouped into three categories based on the structural characteristics such as:



Monoazo dyes
Procion yellow
(Yellow reactive 4)
($C_{20}H_{12}Cl_2N_6Na_2O_6S_2$)

Tartrazine
(Acid yellow 23)
($C_{16}H_9N_4Na_3O_9S_2$)

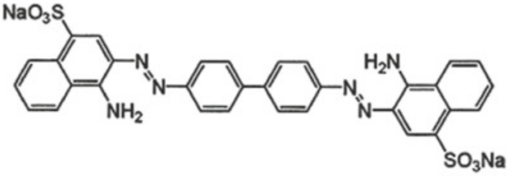
Carmoisine
(Acid red 14)
($C_{20}H_{12}N_2Na_2O_7S_2$)

Allura red
(Food red 17)
($C_{18}H_{14}N_2Na_2O_8S_2$)

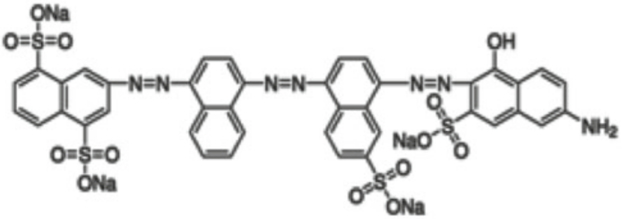
Diazo dyes
Remazol black B
(Black reactive 5)
($C_{26}H_{21}N_5Na_4O_{19}S_6$)

Fig. 4.3 Molecular formula and structure of azo dyes. Note: Molecular formula and structure are taken from the websites: https://www.ncbi.nlm.nih.gov/pccompound and https://images.google.com/

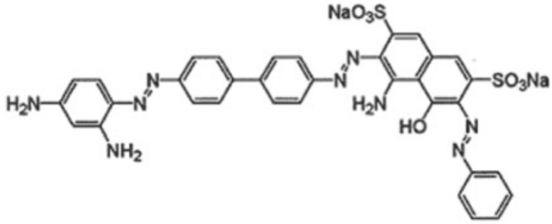
Congo red
(Direct red 28)
($C_{32}H_{22}N_6Na_2O_6S_2$)



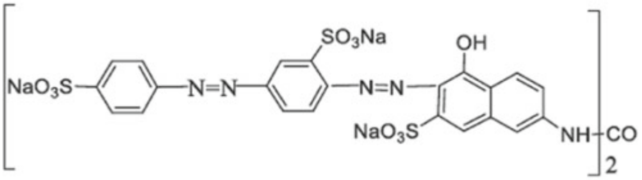
Triazo dyes
Direct blue 71
($C_{40}H_{23}N_7Na_4O_{13}S_4$)



Chlorazol black
(Direct black 38)
($C_{34}H_{25}N_9Na_2O_7S_2$)



Polyazo dyes
Sirius Red
(Direct red 80)
($C_{45}H_{26}N_{10}Na_6O_{21}S_6$)



Direct black 32
($C_{48}H_{40}N_{13}Na_3O_{13}S_3$)

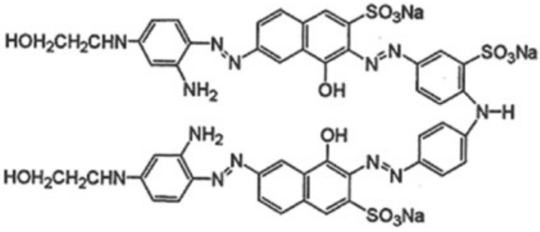
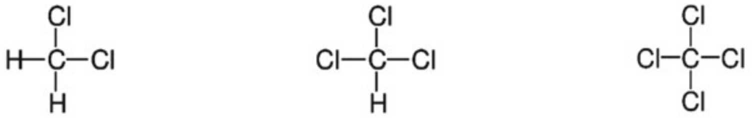
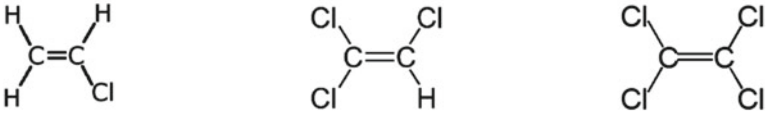


Fig. 4.3 (continued)

1. Chlorinated methane: chloromethane (methyl chloride), dichloromethane (methylene chloride), trichloromethane (chloroform), tetrachloromethane (carbon tetrachloride)
2. Chlorinated ethane: 1,1-dichloroethane, 1,1,1-trichloroethane (methyl chloroform), 1,1,2,2-tetrachloroethane, hexachloroethane (perchloroethane)



Dichloromethane (CH_2Cl_2) Trichloromethane ($CHCl_3$) Tetrachloromethane (CCl_4)



Chloroethene (C_2H_3Cl) Trichloroethylene (C_2HCl_3) Tetrachloroethylene (C_2Cl_4)

Fig. 4.4 Molecular formula and structure of chlorinated solvents, which are carcinogenic. Note: Molecular formula and structure are taken from the websites: https://www.ncbi.nlm.nih.gov/pccompound and https://images.google.com/

3. Chlorinated ethene: chloroethene (vinyl chloride), 1,1-dichloroethylene (vinylidene chloride), trichloroethylene, tetrachloroethylene (perchloroethylene) (Field and Sierra-Alvarez 2004; Guha et al. 2012; Green-Lott et al. 2020) (Fig. 4.4)

These are widely used in the manufacturing industry as degreasing agent (degrease fats, oils, waxes, and resins), paint removers, adhesive solvent, and chemical intermediate and in fire extinguishers and dry-cleaning operations (Guha et al. 2012; Johnson et al. 2017; Green-Lott et al. 2020; Dekant et al. 2021; Dell'Armi et al. 2021). Human exposure to these solvents is mainly through water sources (e.g., parent compounds and TPs) and at workplace (Green-Lott et al. 2020). Chlorinated solvents are hazardous, and most of them are carcinogenic to humans (USEPA 2009; Guha et al. 2012; Green-Lott et al. 2020). For instance, dichloromethane is a probable human carcinogen (biliary tract cancer and non-Hodgkin lymphoma) (USEPA 2009; Benbrahim-Tallaa et al. 2014; IARC (International Agency for Research on Cancer) 2017; Dekant et al. 2021), trichloromethane and tetrachloromethane are possible human carcinogens (IARC 1999), trichloroethylene is a potential human carcinogen (kidney and liver cancer and non-Hodgkin lymphoma), and tetrachloroethylene is a probable human carcinogen (bladder, liver, and lung cancer) (USEPA 2009; Guha et al. 2012; Mattei et al. 2014). These chlorinated solvents are in the priority pollutants list of USEPA (2009), and the maximum contaminant level of dichloromethane, trichloroethylene, tetrachloroethylene, and vinyl chloride in the drinking water is 5 μg/L, 5 μg/L, 5 μg/L, and 2 μg/L, respectively (USEPA 2009). The detailed discussion on the environmental risk of chlorinated solvents in the wastewater and their physicochemical properties can be found in the literature (e.g., USEPA 2009; Benbrahim-Tallaa et al. 2014; IARC 2017; Dekant et al. 2021).

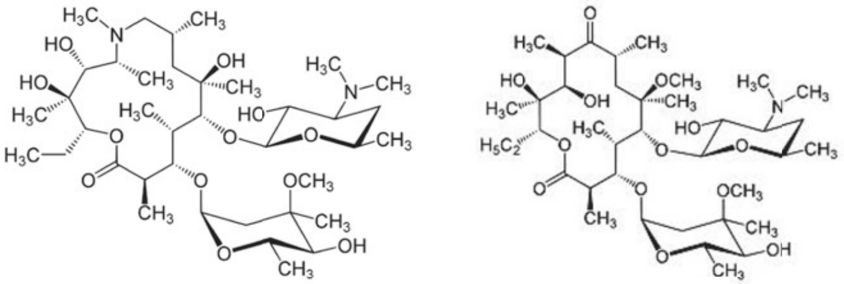
4.2.5 Emerging Organic Contaminants

There are several categories of EOCs such as PhCs, PCPs, SHs, surfactants, industrial chemicals, pesticides, and per- and polyfluoroalkyl substances. In the following sections, four categories of EOCs (PhCs, PCPs, SHs, and pesticides) are discussed in detail.

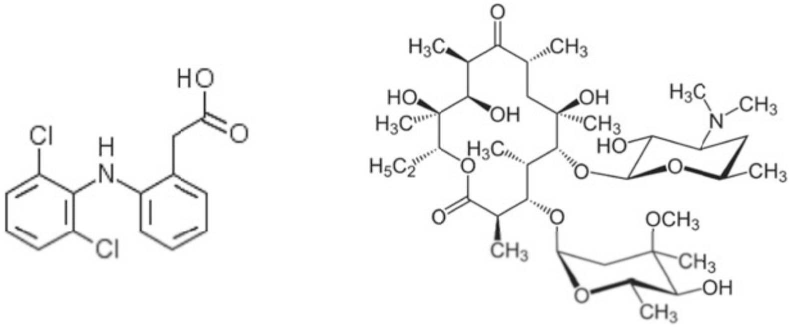
4.2.5.1 Pharmaceuticals

PhCs are discharged to water resources and environment through various sources such as domestic wastewater, hospital and PhCs' industrial waste streams, landfill leachate, runoff from concentrated animal feeding operations and aquaculture, and effluent discharge from WWTPs (Table 4.1). There are several types of PhCs which are categorized according to their therapeutic classes (Ilyas et al. 2020). The most common categories of PhCs are given in Table 4.1. Several studies have indicated the negative impacts of PhCs on aquatic and plant life (e.g., Caliman and Gavrilescu 2009; Carvalho et al. 2014; Gorito et al. 2017). For instance, in WWTPs, during biological treatment, the development of antibiotic-resistant bacteria (ARB) and/or antibiotic resistance genes (ARGs) due to the sub-therapeutic concentrations of antibiotics is of major concern. Antibiotic resistance is the ability of bacteria and other microorganisms to resist the effects of an antibiotic to which they were once sensitive (e.g., Berglund et al. 2014; Liu et al. 2014; Santos et al. 2019). Since these antibiotics, ARB, and ARGs are also not eliminated by conventional WWTPs (e.g., Hijosa-Valsero et al. 2011; Rowan 2011; Huang et al. 2017), the effluent discharge from WWTPs and the use of activated sludge containing antibiotics and ARB/ARGs make them one of the major sources of antibiotics and ARB/ARGs in the environment (Finley et al. 2013; Rodriguez-Mozaz et al. 2015; Santos et al. 2019). Four PhCs including azithromycin, clarithromycin, diclofenac, and erythromycin are on the EU watch list as per EU Decision 2015/495 (EU 2015; Barbosa et al. 2016; Gorito et al. 2017) and EU Decision 2018/840 (EU 2018; Loos et al. 2018) (Fig. 4.5).

Ilyas et al. (2020) estimated the environmental risk posed by widely investigated PhCs as a risk quotient (RQ) (a ratio between the predicted or measured environmental concentration (PEC or MEC) and the worst-case predicted no-effect concentration (PNEC)) (Hernando et al. 2006). Following on the recommendations by Hernando et al. (2006) and several applications (e.g., Verlicchi et al. 2012; Zhu and Chen 2014; Matamoros et al. 2016, 2017; Vymazal et al. 2017), the risk was categorized into four levels: high risk ($RQ > 1.0$), medium risk ($0.1 \leq RQ \leq 1.0$), low risk ($0.01 \leq RQ \leq 0.1$), and no risk ($RQ < 0.01$). Based on influent RQ assessment, 17 out of 27 examined PhCs were grouped under high risk category (diclofenac, ibuprofen, ketoprofen, naproxen, salicylic acid, acetaminophen, clarithromycin, erythromycin, doxycycline, ofloxacin, oxytetracycline, sulfadiazine, sulfamethazine, sulfamethoxazole, carbamazepine, metoprolol, and gemfibrozil). Most of these PhCs are antibiotics and analgesic/anti-inflammatory drugs including the PhCs on the EU watch list. The detailed discussion on the estimated



Azithromycin ($C_{38}H_{72}N_2O_{12}$) Clarithromycin ($C_{38}H_{69}NO_{13}$)



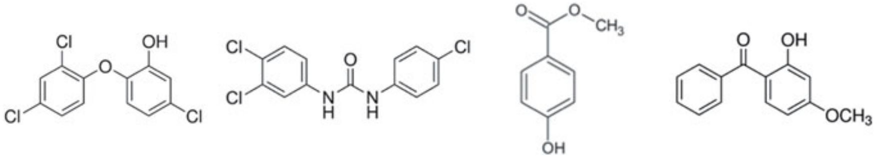
Diclofenac ($C_{14}H_{11}Cl_2NO_2$) Erythromycin ($C_{37}H_{67}NO_{13}$)

Fig. 4.5 Molecular formula and structure of pharmaceuticals (PhCs), which are on the EU watch list. Note: Molecular formula and structure are taken from the websites: https://www.ncbi.nlm.nih.gov/pccompound and https://images.google.com/

environmental risk of the examined PhCs in the influent wastewater and their physicochemical properties can be found in Ilyas et al. (2020).

4.2.5.2 Personal Care Products

PCPs are discharged to water resources and environment through various sources such as domestic and industrial wastewater, landfill leachate, and effluent discharge from WWTPs (Table 4.1). There are several types of PCPs which are categorized according to their uses (Ilyas and van Hullebusch 2020a). The most common categories of PCPs are given in Table 4.1. It has been indicated that higher concentration of PCPs compared with their potential no-effect concentration could pose severe risk to human health, since many of these PCPs are considered as prospective EDCs (Caliman and Gavrilescu 2009; Gogoi et al. 2018). For instance, triclosan (molecular formula, $C_{12}H_7C_{13}O_2$), which is a broad-spectrum synthetic antimicrobial used in PCPs such as toothpaste, mouthwash, antibacterial soaps (bars and liquids), deodorant, cleansers, hand sanitizers, and medical disinfectants, has been frequently found in wastewater and drinking water (Singer et al. 2002; Witorsch and Thomas 2010; Dann and Hontela 2011; Yueh and Tukey 2016). It is categorized as a halogenated aromatic hydrocarbon and contains phenolic, diphenyl ether, and



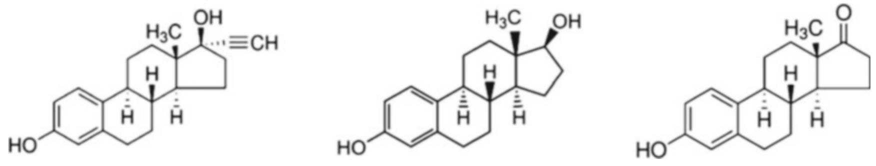
Triclosan ($C_{12}H_7Cl_3O_2$) Triclocarban ($C_{13}H_9Cl_3N_2O$) Methylparaben ($C_8H_8O_3$) Oxybenzone ($C_{14}H_{12}O_3$)

Fig. 4.6 Molecular formula and structure of high-risk personal care products (PCPs). Note: Molecular formula and structure are taken from the websites: https://www.ncbi.nlm.nih.gov/pccompound and https://images.google.com/

polychlorinated biphenyl (PCB) substructures (e.g., Ahn et al. 2008); hence, the chemical properties are related to many toxic compounds such as PCBs, polybrominated diphenyl ethers, bisphenol A, and dioxins (e.g., Allmyr et al. 2008). Toxicological studies suggest the negative effects of triclosan on human and animal health such as the impact on endocrine function, thyroid hormone homeostasis, and antibiotic resistance (e.g., Witorsch and Thomas 2010; Dhillon et al. 2015; Yueh and Tukey 2016). Therefore, the widespread exposure of human and negative impacts of triclosan on human health make this compound an EOC of interest and focus of research (Goodman et al. 2018). Ilyas and van Hullebusch (2020a) estimated the environmental risk posed by widely investigated PCPs as a RQ. Based on influent RQ assessment, 4 out of 11 examined PCPs were grouped under high risk category including triclosan and triclocarban (antiseptics), methylparaben (preservatives), and oxybenzone (sunscreen agents) (Fig. 4.6). The detailed discussion on the estimated environmental risk of the widely investigated PCPs in the wastewater and their physicochemical properties can be found in Ilyas and van Hullebusch (2020a).

4.2.5.3 Steroidal Hormones

SHs are discharged to water resources and environment through various sources such as domestic and industrial wastewater, runoff from concentrated animal feeding operations and aquaculture, landfill, and effluent discharge from WWTPs (Table 4.1). There are several types of SHs which are categorized based on their structural characteristics and pharmacological effects. The most common categories of SHs are given in Table 4.1. SHs are among the EOCs that are considered as prospective EDCs (Caliman and Gavrilescu 2009; Töre et al. 2012; Gogoi et al. 2018). Therefore, the occurrence of SHs has raised an increasing concern and research interest in the last decade due to their possible toxicological effects to the environment and living organisms (Barbosa et al. 2016; Adeel et al. 2017; Biswas et al. 2017; Gogoi et al. 2018), even at very low concentrations (0.1–0.5 ng/L) (Adeel et al. 2017). For instance, estrogens (EDCs) existing either as natural substances (estriol, estrone, and 17β-estradiol) or synthetic substances (17-α-ethinylestradiol, used as oral contraceptive) that are mainly excreted by humans are found in the aquatic environment (Rocha et al. 2008; Sun et al. 2013; Barreiros



17α-ethinylestradiol ($C_{20}H_{24}O_2$) 17β-estradiol ($C_{18}H_{24}O_2$) Estrone ($C_{18}H_{22}O_2$)

Fig. 4.7 Molecular formula and structure of steroidal hormones (SHs), which are on the EU watch list. Note: Molecular formula and structure are taken from the websites: https://www.ncbi.nlm.nih.gov/pccompound and https://images.google.com/

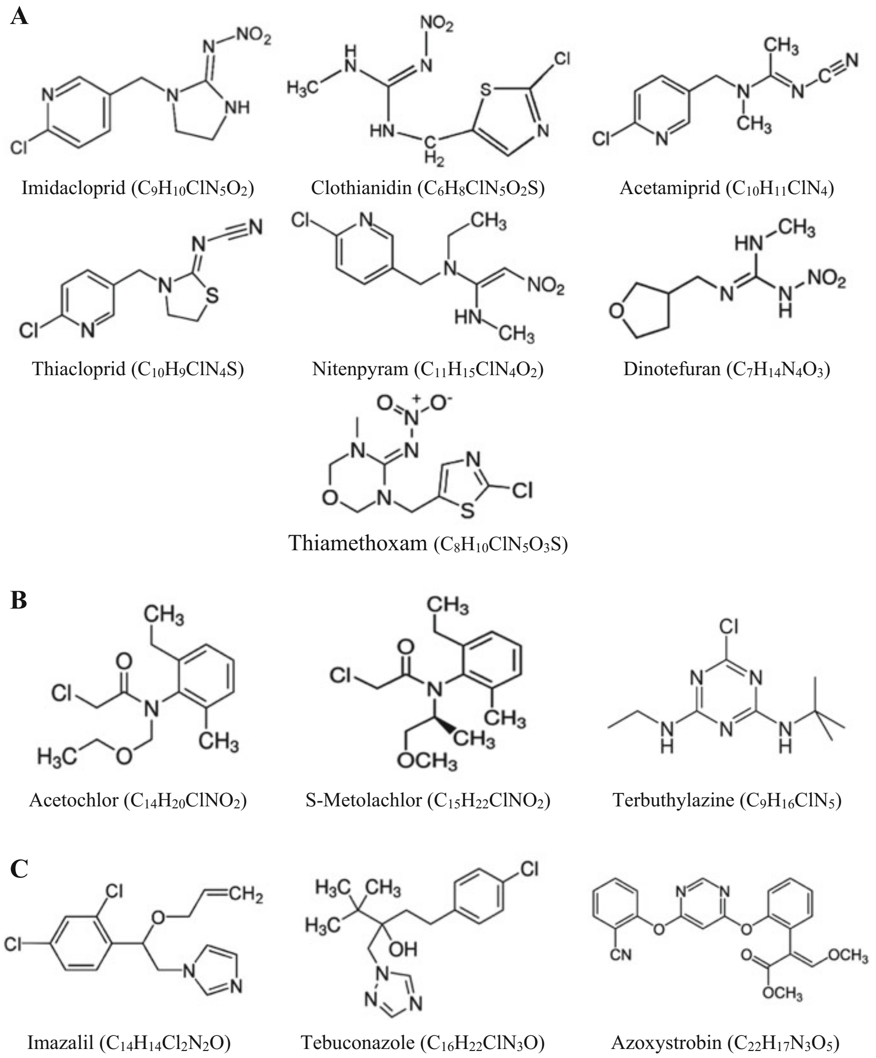
et al. 2016). These estrogens cause adverse effects to the ecosystems such as feminization of male fishes and DNA and immunity alterations (Purdom et al. 1994; Länge et al. 2001; Kidd et al. 2007; Li 2014; Leet et al. 2015). Similarly, the progestogen such as levonorgestrel is usually associated with 17-α-ethinylestradiol in contraceptive pills and is known to have androgenic effect, which leads to masculinization in fish (Pu et al. 2008; Kloas et al. 2009; Leet et al. 2015; Runnalls et al. 2015). Norethisterone also known as norethindrone (progestogen) is used for hormone regulation, endometriosis, and chronic pelvic treatment (Simon et al. 2003; Chawla 2010; Kaser et al. 2012). Although it is not frequently found in natural environment, some studies have revealed the potential transformation of norethindrone to 17α-ethinylestradiol (e.g., Kuhnz et al. 1997). Furthermore, EDCs are of profound concern as some studies suggested that long-term exposure to them could pose severe risk to human health, which includes a decrease in male sperm count; an increase in testicular, prostate, ovarian, and breast cancers; and reproductive malfunctions (e.g., Joffe 2001; Sharpe and Irvine 2004). Three estrogens, namely, 17α-ethinylestradiol, 17β-estradiol, and estrone, are on the EU watch list as per EU Decision 2015/495 (EU 2015; Barbosa et al. 2016; Gorito et al. 2017) and EU Decision 2018/840 (EU 2018; Loos et al. 2018) (Fig. 4.7).

Barbosa et al. (2016) summarized the available data and the concentration of these three estrogens. The concentration of 17α-ethinylestradiol, 17β-estradiol, and estrone in different aquatic compartments, including effluents of wastewater, surface water, and groundwater, was estimated from the data reported in the case studies from nine countries across different regions of the world (China, Korea, Japan, South Africa, Sweden, France, Germany, the UK, and the USA). The estimated average concentration of 17α-ethinylestradiol in wastewater, surface water, and groundwater was up to 0.008 μg/L, 0.002 μg/L, and 0.23 μg/L, respectively. The corresponding concentration of 17β-estradiol was 0.09 μg/L, 0.01 μg/L, and 0.15 μg/L, respectively, and that of estrone was 0.22 μg/L, 0.07 μg/L, and 0.08 μg/L, respectively (Barbosa et al. 2016). Ilyas and van Hullebusch (2020b) estimated the environmental risk posed by widely investigated SHs as a RQ. Based on influent RQ assessment, seven out of nine examined SHs could be grouped under high risk category including 17α-ethinylestradiol, 17β-estradiol, estrone, and estriol (estrogens), norethisterone (progestogens), and androstenedione and testosterone (androgens). The detailed discussion on the estimated environmental risk of the widely investigated SHs in the wastewater and their physicochemical properties can be found in Ilyas and van Hullebusch (2020b).

4.2.5.4 Pesticides

Pesticides are grouped into three categories such as insecticides, herbicides, and fungicides (Luo et al. 2014; Vymazal and Březinová 2015). All these categories of pesticides are discharged to water resources and the environment through various sources such as agricultural runoff, domestic and industrial wastewater, landfill leachate, and effluent discharge from WWTPs (Table 4.1). The insecticides are classified into several groups (neonicotinoids, sulfoximines, mesoionics, carbamates, organophosphates, pyrethroids, and insect growth regulators) (Stehle et al. 2018; Zhang et al. 2018a; Liao et al. 2021; Tudi et al. 2021). The most widely used class of insecticides is neonicotinoids (e.g., imidacloprid, clothianidin, acetamiprid, thiacloprid, nitenpyram, dinotefuran, and thiamethoxam) (e.g., Todey et al. 2018; Yin et al. 2018; Lee et al. 2020; Berens et al. 2021). The seven currently available and widely used neonicotinoids can be classified into three cyclic groups, five-membered ring systems (imidacloprid and thiacloprid), six-membered systems (thiamethoxam), and noncyclic compounds (nitenpyram, acetamiprid, clothianidin, and dinotefuran) (Fig. 4.8a). Neonicotinoids are effective and have the same mode of action toward most of the agricultural, urban, and household pests (e.g., mites, coleopterans, aphids, whiteflies) (e.g., Matsuda et al. 2001). These are most frequently detected with the highest concentrations at agricultural locations than urban and undeveloped regions. Among them, clothianidin and imidacloprid were closely associated with agricultural and urban land use, respectively (Berens et al. 2021). Although these are generally not toxic to wildlife and humans (Tomizawa and Casida 2005; USEPA 2018), these can pose adverse effects on nontarget pollinators (e.g., honeybees, Lepidoptera), insects (e.g., Ephemeroptera, Trichoptera), plankton (e.g., copepods, *Daphnia*), and freshwater vertebrates and macrophytes (Goulson 2013; Bonmatin et al. 2015; Gibbons et al. 2015; USEPA 2020).

Herbicides are classified into different groups based on their chemical structure, way of translocation, mechanism of action, and herbicidal activity (Damalas and Eleftherohorinos 2011; Nefed'eva et al. 2021). Among them, chloroacetanilide herbicides (acetochlor, *s*-metolachlor, metazachlor, dimethachlor) (Chen et al. 2017b) and triazine herbicides (terbuthylazine) (Gikas et al. 2018; Tudi et al. 2021) are used to control annual grasses and broadleaved weeds in a variety of crop (e.g., corn, barley, wheat, sorghum, asparagus, peaches, grape, apple, banana, pineapple, citrus, sugarcane, coffee, and maize) (Barceló 1991; Lewis et al. 2016; Chen et al. 2017b). Acetochlor and *s*-metolachlor (substitutes of alachlor and *r*-metolachlor, respectively) are among the ten most commonly used herbicides in Europe and the USA (USEPA 2011) (Fig. 4.8b). Therefore, chloroacetanilide herbicides and their TPs such as ethane sulfonic acids and oxanilic acids are often detected in the surface and groundwater (e.g., Hladik et al. 2005; Baran and Gourcy 2013). Acetochlor is classified as potential human carcinogen (USEPA 2018). Terbuthylazine is also used for nonagricultural purposes such as forestry and maintenance of roads (Barceló 1991; Lewis et al. 2016) and was used as a substitute



Imidacloprid ($C_9H_{10}ClN_5O_2$)
Clothianidin ($C_6H_8ClN_5O_2S$)
Acetamiprid ($C_{10}H_{11}ClN_4$)
Thiacloprid ($C_{10}H_9ClN_4S$)
Nitenpyram ($C_{11}H_{15}ClN_4O_2$)
Dinotefuran ($C_7H_{14}N_4O_3$)
Thiamethoxam ($C_8H_{10}ClN_5O_3S$)

Acetochlor ($C_{14}H_{20}ClNO_2$)
S-Metolachlor ($C_{15}H_{22}ClNO_2$)
Terbuthylazine ($C_9H_{16}ClN_5$)

Imazalil ($C_{14}H_{14}Cl_2N_2O$)
Tebuconazole ($C_{16}H_{22}ClN_3O$)
Azoxystrobin ($C_{22}H_{17}N_3O_5$)

Fig. 4.8 Molecular formula and structure of widely used insecticides (**a**), herbicides (**b**), and fungicides (**c**). Note: Molecular formula and structure are taken from the websites: https://www.ncbi.nlm.nih.gov/pccompound and https://images.google.com/

of atrazine due to its prohibition in the EU (Gikas et al. 2018) (Fig. 4.8b). Terbuthylazine is considered as the most persistent triazine herbicide in the surface water (Pinto et al. 2012), and its occurrence in the water resources is of global concern (Du Preez et al. 2005; Claver et al. 2006), which necessitates to improve agricultural runoff water quality (Chen et al. 2017b). Furthermore, herbicides accounted for the largest portion of the total use of pesticides followed by insecticides and fungicides (USEPA 2011).

Among the most widely used fungicides in agriculture for crop protection are azole fungicides such as triazole (e.g., tebuconazole, difenoconazole, propiconazole, and hexaconazole) (Lyu et al. 2018; Cao et al. 2021; Toda et al. 2021) and imidazole (imazalil and prochloraz) (Lv et al. 2016; Jørgensen et al. 2021; Yang et al. 2021) and non-azole fungicides (fluopyram, azoxystrobin, and fluxapyroxad) (Feng et al. 2020; Podbielska et al. 2020; Sun et al. 2020; Jørgensen et al. 2021; Li et al. 2021) (Fig. 4.8c). Tebuconazole is a triazole fungicide, which is used other than antifungal activities (Shikuku et al. 2014) as an active ingredient in wood preservatives (e.g., Miyauchi et al. 2005). Most of these fungicides are toxic to aquatic life and human health (EFSA 2014; USEPA 2018) and are classified as possible human carcinogen (hexaconazole, tebuconazole, propiconazole, imazalil, and prochloraz) and potential human carcinogen (difenoconazole) (USEPA 2018). The detailed discussion on the environmental risk of the widely investigated pesticides in the wastewater and their physicochemical properties can be found in the literature (e.g., Lv et al. 2016; Chen et al. 2017b; Gikas et al. 2018; Lyu et al. 2018; USEPA 2018; Lee et al. 2020).

4.3 Description of Inorganic Contaminants

4.3.1 Metal(loid)s

Uncontrolled discharge of metals and metalloids as inorganic pollutants has become a worldwide critical problem in recent years. A few potentially toxic metal(loid)s (e.g., manganese (Mn), Cu, Zn, cobalt (Co), and selenium (Se)) are known as micronutrients due to their biological importance on living organisms; however, majority of them are toxic in nature particularly at high concentrations (e.g., cadmium (Cd), chromium (Cr), lead (Pb), arsenic (As), Se, and mercury (Hg)) (Pathak et al. 2020; Sharma et al. 2021). Various anthropogenic activities like mining, extraction or refining ores, and agricultural drainage due to use of pesticides and chemical fertilizers and various industries including petrochemicals, dyes and paints, PhCs, tanning, paper and pulp, alloys or metal plating, automobiles, and battery industries are mainly responsible for the exponential increase of metals' and metalloids' discharge and environmental pollution, while coal-based thermal power plants alone release majority of metal(loid)s including As, Se, Hg, Cd, Cr, Pb, Zn, Co, and Ni in high concentrations causing environmental pollution (Choudhary et al. 2017; Tanmoy and Saha 2019; Hirvaniya et al. 2021). As PTMs are naturally present in the Earth's crust, PTMs' pollution in the environment can occur via natural processes also including volcanic eruptions and weathering of rocks and minerals. For example, Se can be released due to the weathering of seleniferous rocks and sediments; similarly dissolution of As from naturally occurring geologic deposits can cause As pollution into groundwater (Tanmoy and Saha 2019).

Being persistent and non-degradable, these can remain in the environmental settings after their release into the environment for decades or centuries. PTMs can eventually enter the food chain through the roots of plants or aquatic organisms, thus causing concern of possible long-term environmental impacts and human health (Chowdhury et al. 2016; Sharma et al. 2021). PTMs can be extremely poisonous, moderately poisonous, and slightly poisonous depending on their toxicity (Table 4.2). Among them, Cr, Pb, Cd, As, and Hg are the priority toxic metals due to their carcinogenic nature and are of primary concern for the public health (Dixit et al. 2015; Choudhary et al. 2017; Sharma et al. 2021). PTMs cause cell toxicity associated with various mechanisms: (1) the production of reactive oxygen species disrupting the DNA structure and cell membrane; (2) affecting the function of DNA repair as well as formation of protein; (3) deregulating enzyme activity and function; (4) causing ion imbalance by adhering to the cell surface and entering through ion channels or transmembrane carrier; and (5) deactivating cellular functions inducing cell death (Dixit et al. 2015; Choudhary et al. 2017; Sharma et al. 2021). Furthermore, PTMs can be bioaccumulated and affect various organs including the nervous system, hematopoietic system, cardiovascular system, renal system, and reproductive system in aquatic organisms (Table 4.2). PTMs can also interact with organic compounds to form toxic metal-organic complex. For example, Cr can interact with carboxyl and thiol groups of enzymes and change the enzyme structure and activity (Dixit et al. 2015; Sharma et al. 2021).

4.3.2 Radionuclides

Radionuclide contamination in the environment has been detected around the world and considered as a major environmental and human health concern. Radionuclide pollution can occur via various activities: (1) uranium (U) mining and milling, (2) nuclear fuel reactor facilities and operation of nuclear power plants, (3) testing nuclear power weapons, (4) disposal of nuclear wastes, (5) drilling and production of oil and gas, (6) coal combustion, and (7) phosphate mining and extraction of rare-earth elements (Das 2012; Francis and Nancharaiah 2015; Shukla et al. 2017). Fatal nuclear power plant accidents such as Chernobyl disaster in 1986 and the Fukushima Daiichi nuclear disaster of 2011 are also among the source of introduction of radionuclides into the environment. In addition, broad application of radioactive materials at various research including biomedical and industrial application is also responsible for the discharge of radioactive waste into the environment around the world (Prakash et al. 2013).

As radionuclides have a very long half-life, it can have the hazardous impact in the environment for a prolonged period of time even at a small concentration. The most concerning radioactive elements found in the environments are the U-238 (^{238}U), radon-222 (^{222}Rn), technetium-99 (^{99}Tc), plutonium-239 (^{239}Pu), thorium-232 (^{232}Th), and cobalt-60 (^{60}Co) which show high radiotoxicity with most of them having very long half-lives (Das 2012; Francis and Nancharaiah 2015). ^{232}Th, ^{235}U, and ^{238}U decay series are commonly found in high concentrations in deep water wells present in the close proximity of U deposit, while ^{238}U, ^{232}Th, ^{222}Rn, and radium-226 (^{226}Ra) are found in groundwater mostly (Das 2012). Other radionuclides including iridium-192 (^{192}Ir), thallium-201 (^{201}Tl), strontium-90

(^{90}Sr), and cesium-137 (^{137}Cs), which are produced via nuclear reactors during the atom splitting, also have a significantly long decay time (Kurnaz et al. 2007). Other naturally occurring radionuclide elements are of less concern as they are present in very small amount in the natural environmental settings and have shorter decay time (Francis and Nancharaiah 2015).

Water pollution with the radionuclides is a major concern because of their radioactivity and high toxicity even at low concentration. Specially, the oxidation of radionuclide in natural environmental settings is a serious threat as some radionuclides become more toxic and more soluble into the aquatic environment (Das 2012). This can lead to the higher mobilization of toxic radionuclide elements and more contamination of the surface water and groundwater causing potential hazardous consequences toward aquatic environment and human health (Macaskie 1991; Tabak et al. 2005; Das 2012). The radionuclides can emit alpha, beta, or gamma radiation which can inhibit the microbial reproduction by inducing the DNA alteration leading to the DNA degradation via direct and/or indirect methods (Shukla et al. 2017). The detrimental effects occur on the core nuclear material of any cell—the DNA. An electron can be ejected directly out of the DNA due to ionizing radiations, while DNA damaging by indirect mechanisms involved the radiolysis of DNA (Ravanat and Douki 2016).

Long-term exposure to radiation can cause infertility, birth defects, neurological disorders, and cancers in various organs including the colon, esophagus, ovary, breast, lung, and stomach (Das 2012; Prakash et al. 2013; Shukla et al. 2017). They can also pose serious threat if applied excessively on living things during any medical treatment which is known as radiation poisoning (Das 2012). With increasing exposure, one can experience nausea, vomiting, fatigue, fever, headaches, hair loss, and eventually death. Particularly, fetuses are susceptible to the radiation at the cellular level, resulting in various abnormalities including smaller brain size and mental retardation, eye deformation, abnormal growth, and other serious health-related issues due to genetic damage, which can pass to the next generation as well (Mohner et al. 2006; Nussbaum 2007; Prakash et al. 2013).

4.4 Biotechnology Applications

Several physicochemical and biological treatment technologies are applied to remediate organic and inorganic contaminants from the wastewater (Crini and Lichtfouse 2019; Khalid et al. 2021). Among the physicochemical remediation techniques are coagulation/flocculation, adsorption, precipitation, vapor extraction, flotation, ion exchange, enzymatic degradation, membrane technologies, and advanced oxidation processes (e.g., Fenton, ultraviolet irradiation, hydrogen peroxide, and ozone) (Aplin and Waite 2000; Kim et al. 2002; Ukiwe et al. 2014; De Gisi et al. 2016; Wang and Zhuang 2018; Crini and Lichtfouse 2019; Ezugbe and Rathilal 2020). All the physicochemical methods have advantages and limitations in their application for the treatment of wastewater. Although physicochemical methods of wastewater treatment are easy to use, these methods are costly and are not environmentally friendly, which limit their extended utilization (De Gisi et al. 2016; Bhatia et al. 2017; Sarkar et al. 2017; Crini and Lichtfouse 2019; Ijanu et al. 2020). This indicates the need for wastewater treatment technologies, which are sustainable and can be used to remove organic and inorganic contaminants from the wastewater in a cost-effective and environmentally friendly manner such as bioremediation techniques (Montero-Rodríguez et al. 2015; Pandey et al. 2019; Fayyad et al. 2020; Ahmad et al. 2021; Banerjee 2021).

4.4.1 Bioremediation

Bioremediation is an environmentally friendly, cost-effective, and sustainable technique to reestablish the deteriorated environments (soil, sediments, water, and air) (e.g., Kulshreshtha et al. 2014; Adams et al. 2015; Vijayalakshmi et al. 2018; Kumar and Bharadvaja 2019; Khalid et al. 2021). Bioremediation involves the use of living organisms such as naturally occurring bacteria, fungi, algae, and plants to degrade or detoxify organic and inorganic contaminants, which pose risk to aquatic organisms and human health. There are several types of bioremediation methods such as microbial remediation (microbes (e.g., bacteria)) (Vidali 2001; Kumar et al. 2011; Adams et al. 2015; Arora and Vanza 2017; Khalid et al. 2021), mycoremediation (fungi) (Kumhomkul and Panich-pat 2013; Purnomo et al. 2013; Kulshreshtha et al. 2014; Kumar and Dwivedi 2021), phycoremediation (algae) (Pandey et al. 2019; Ahmad et al. 2021), and phytoremediation (plants) (Vidali 2001; Afzal et al. 2019; Ilyas and van Hullebusch 2020a, b; Ilyas et al. 2020).

There are two types of bioremediation strategies based on the removal and transportation of wastes for the treatment: in situ and ex situ bioremediation. In situ bioremediation techniques are applied to soil and groundwater at the site with minimal disturbance, whereas ex situ techniques are applied to soil and groundwater at the site that has been removed from the site by excavation (soil) or pumping (water) (Vidali 2001; Kumar et al. 2011). Among the in situ bioremediation techniques, the most commonly used are bioventing, biosparging, in situ biodegradation, and bioaugmentation. The ex situ bioremediation is classified as solid phase system (including land treatment and soil piles) and slurry phase systems (including solid-liquid suspensions in bioreactors). The most widely applied ex situ bioremediation techniques are land farming, composting, biopiles, and bioreactors (Vidali 2001; Kumar et al. 2011).

4.4.1.1 Microbial Remediation

Microbial remediation involves the use of microorganisms (e.g., bacteria) to degrade, reduce, eliminate, or transform the contaminants present in soils, sediments, water, and air (Adams et al. 2015; Horel and Schiewer 2020). Mostly microbial degradation takes place under aerobic conditions; however, the anaerobic conditions might be favorable for microbial degradation of recalcitrant organic compounds (Vidali 2001; Kumar et al. 2011). The efficiency of microbial degradation is influenced by the growth and degradation rate of microorganisms, and several factors contribute to their performance in utilizing organic contaminants such as temperature, pH, salinity, and nitrogen and carbon sources (Vidali 2001; Khalid et al. 2021).

Bacteria are extensively investigated for the treatment of wastewater containing organic contaminants such as PAHs and petroleum hydrocarbons (Sanches et al. 2017; Wongbunmak et al. 2020; Al-Mur et al. 2021; Zhang et al. 2021). Al-Mur et al. (2021) investigated the biodegradation of PAHs including pyrene, benzo (e)pyrene, benzo(k)fluoranthene, and benzo(a)pyrene by the extremophilic consortium that possessed *Ochrobactrum*, *Bacillus*, *Marinobacter*, *Pseudomonas*, *Martelella*, *Stenotrophomonas*, and *Rhodococcus* under optimized extreme condition. The degradation of pyrene, benzo(e)pyrene, benzo(k)fluoranthene, and benzo (a)pyrene was 93%, 60%, 55%, and 51%, respectively. Besides biodegradation, Sanches et al. (2017) reported the biosorption of PAHs such as acenaphthene and phenanthrene to the anaerobic microbial consortium composed of *Diaphorobacter* and *Paracoccus* genera. The results showed that 77% of acenaphthene was removed within 17 h, whereas phenanthrene was removed 83% within 12 h and was below the limit of detection after 15 h. Wongbunmak et al. (2020) examined a non-pathogenic, Gram-positive rod-shaped bacterium *Bacillus amyloliquefaciens* W1 to degrade all the six BTEX compounds. The removal efficiency of benzene, toluene, ethylbenzene, *para*-xylene, *meta*-xylene, and *ortho*-xylene was 29%, 34%, 29%, 30%, 18%, and 14%, respectively. Biodecolorization and biodegradation have been investigated for the treatment of wastewater containing azo dyes to decolorize and degrade them (Tom-Sinoy et al. 2011; Saini 2017; Sarkar et al. 2017; Mhatre 2021). Tom-Sinoy et al. (2011) examined the potential of aerobic mixed culture of *Pseudomonas* spp. and *E. coli* for decolorization of carbol fuchsin dye, and the mixed culture could achieve the decolorization up to 91% after 24 h of incubation period at pH 7–8 and temperature 30 °C. However, the study by Mhatre (2021) revealed that various optimal conditions (pH, 7; temperature, 37 °C; carbon source, glucose; and nitrogen source, ammonium chloride (NH_4Cl) and peptone) can increase the performance of *Acinetobacter* spp. for carbol fuchsin dye decolorization (94% within 24 h). Several studies examined the biological treatment of wastewater containing chlorinated solvents to explore the potential of bacteria for their degradation (van Eekert and Schraa 2001; Priya and Philip 2013; Varzaghani et al. 2021). Varzaghani et al. (2021) investigated the biodegradability of tetrachloroethylene (perchloroethylene) (concentration range, 40–760 μM) by *Sphingopyxis ummariensis* bacteria in both suspended and immobilized culture systems under aerobic conditions. The results showed the degradation of tetrachloroethylene from 100% to 80% with an increase in its concentration from 40 to 760 μM.

Biotransformation of PhCs, PCPs, and SHs by ammonia-oxidizing bacteria (e.g., *Nitrosomonas europaea*) was investigated in wastewater treatment processes (Shi et al. 2004; Roh et al. 2009; Xu et al. 2016; Wu et al. 2021). Roh et al. (2009) examined the biodegradation of PhCs (ibuprofen) and PCPs (triclosan) by *Nitrosomonas europaea* and mixed ammonia-oxidizing bacteria in nitrifying activated sludge. The authors reported the high removal efficiency of triclosan (ranging from 90% to 100%) within 5 days and complete removal of ibuprofen

(100%) within 2 days. Lee et al. (2012) reported the higher biodegradation of triclosan (90% within 24 h) by *Sphingopyxis* strain KCY and complete removal (100%) within 2 days. Shi et al. (2004) investigated the degradation of SHs including estrone, 17β-estradiol, estriol, and 17α-ethinylestradiol with the use of nitrifying activated sludge and ammonia-oxidizing bacterium *Nitrosomonas europaea*. The authors reported that other than *Nitrosomonas europaea*, heterotrophic bacteria have also participated in the removal of 17β-estradiol in the enriched nitrifying sludge. Bacteria are also investigated for the treatment of wastewater containing pesticides (Baghapour et al. 2013; Saleh et al. 2020; Zhang et al. 2020). Baghapour et al. (2013) studied the biodegradation of atrazine from aquatic environment by consortium of microorganisms using submerged biological aerated filter. The removal efficiency of atrazine was 72%, 80%, 88%, and 98% with the initial atrazine concentration of 0.01 mg/L, 0.1 mg/L, 1.0 mg/L, and 10 mg/L, respectively, after 24 h. Zhang et al. (2020) examined the biodegradation of triazophos, methamidophos, and carbofuran by *Enterobacter* sp. Z1. The removal efficiency of triazophos, methamidophos, and carbofuran was 98%, 100%, and 99%, respectively, in a batch bioreactor, and under the optimum conditions (temperature, 37 °C; pH, 7; concentration, 100 mg/L of each pesticide), the corresponding removal efficiency was 100%, 100%, and 95%, respectively.

Bacteria have been widely explored for PTM bioremediation due to their small size, ease of cultivation, and quick growth rate. Bacteria are not only the most abundant microorganisms; they can also survive in a wide range of extreme environmental situation (Shukla et al. 2017; Yin et al. 2019; Mal and Rangabhashiyam 2021). The processes by which bacteria can mediate the removal or detoxification of potentially toxic metal(loid)s from agricultural soil are presented in Fig. 4.9. Several bacteria with metal tolerance capability including *Bacillus*, *Pseudomonas*, *Escherichia*, and *Micrococcus* have been successfully explored for the bioremediation of PTMs from the environment (Shukla et al. 2017; Yin et al. 2019; Mal and Rangabhashiyam 2021). *Bacillus cereus* showed high resistance toward Pb (II) toxicity and was able to remove 97% of Pb(II) at pH 7.0 and 35 °C (Anusha and Natarajan 2020). *Bacillus* sp. PZ-1 and *Pseudomonas* sp. I3 have been reported for the removal of Pb(II) from the wastewater via biosorption (Ren et al. 2015; Li et al. 2017b). *Pseudomonas aeruginosa*, being a Hg-resistant strain, can help in selective adsorbing and removing Hg ion from multi-metal pollution source as the Hg ion gets accumulated by cysteine-rich transport proteins available abundantly in sulfhydryl groups (Yin et al. 2016). Cr(VI) adsorption with high removal capacity by both dead and living *Arthrobacter viscosus* biomass has been reported under acidic condition (Yin et al. 2016). Similarly, Cd(II) removal was also reported by using both dead and living cells of *Bacillus cereus* RC-1, with having 32 mg/g and 24 mg/g of biosorption capacity for living and dead cells, respectively (Huang et al. 2013). *Eichhornia* spp. isolated from Chandola Lake were successfully explored for the removal of Cu with 85% removal efficiency, and *Rhodobacter capsulatus* was used for the Zn(II) removal with a maximal uptake capacity of 164 mg Zn/g biomass (Yin et al. 2019). Zhang et al. (2012) demonstrated bioremediation of mercury pollution by complete adsorption and reduction of Hg(II) to Hg(0) using *Pseudomonas putida*

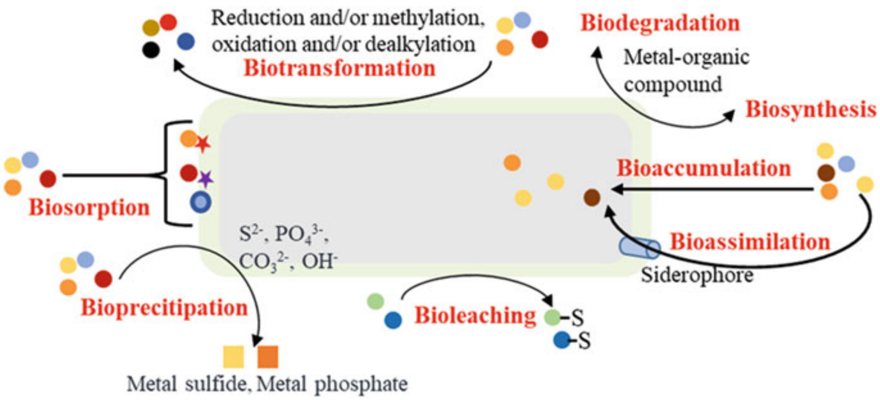


Fig. 4.9 Microbial bioremediation. Processes by which bacteria can mediate the removal or detoxification of potentially toxic metal(loid)s from agricultural soil. Bacteria can interact with potentially toxic metal(loid)s directly, accumulating them on the cell surface (biosorption). They can also reduce or oxidize metal(loid) species and synthesize or degrade metal-containing organic compounds via catalytic reactions (biosynthesis or biodegradation). Sulfur-oxidizing bacteria can release acids and dissolve metal-containing compounds for leaching of metals (bioleaching). Sulfate-reducing bacteria can precipitate metals by formation of low-mobility sulfides (bioprecipitation). Bacteria can also accumulate metals in the intracellular space by using proteins in their cellular processes (bioaccumulation). Bacteria assimilate metals via iron assimilation pathways using siderophores (bioassimilation). Carbonate (CO_3^{2-}), hydroxyl (OH^-), phosphate (PO_4^{3-}), sulfide (S^{2-}). (Adapted from Hou et al. 2020)

SP1 collected from the marine environment. Another example of bioremediation of PTMs via biotransformation is simultaneous reduction of Cr(VI) and oxidation of As (III) by using *Bacillus firmus* TE7 (Yin et al. 2019). Bioreduction of Se oxyanions to nontoxic Se(0) by using pure culture (e.g., *Bacillus selenitireducens*, *Veillonella atypica*, *Pseudomonas stutzeri* NT-1) (Eswayah et al. 2016) or mixed culture (anaerobic and aerobic granular sludge) has been reported extensively (Mal et al. 2017; Wadgaonkar et al. 2018; Tan et al. 2019).

Bacteria have also been widely explored for the removal of radionuclide, especially U via biosorption or biotransformation (Das 2012; Shukla et al. 2017). U (VI) uptake by using *Pseudomonas aeruginosa* CSU was demonstrated by Hu et al. (1996). Microorganisms capable of reducing radionuclide are of particular interest for the dissimilatory reduction of radionuclide coupled with energy conservation. For example, *Geobacter sulfurreducens* strain PCA, *G. metallireducens*, and *Shewanella putrefaciens* strain CN-32 were reported for the bioreduction and immobilization of U(VI) (Das 2012; Shukla et al. 2017). *P. fluorescens* showed strong biosorption capacity and removed 85% of 4.75 mM neptunium (Np(V)) from the solution (Das 2012; Shukla et al. 2017). Bioreduction of Np(V) to insoluble Np (IV) and Pu(VI) and Pu(V) to Pu(IV) by microbes has also been reported (Das 2012; Shukla et al. 2017; Ding et al. 2019). Similarly, bioaccumulation of Cs and Sr has also been reported by using different microorganisms (Ding et al. 2019).

4.4.1.2 Mycoremediation

Mycoremediation is based on the use of fungi and mushroom for the removal of contaminants (organic and inorganic) from the wastewater because the mushrooms and other fungi possess enzymatic machinery for their degradation (Purnomo et al. 2013; Kulshreshtha et al. 2014; Ariste et al. 2020; Kumar and Dwivedi 2021). Mycoremediation of pollutants can be done in in situ and ex situ conditions (Kulshreshtha et al. 2014; Fayyad et al. 2020). Several studies emphasized the role of mushroom and other fungi in bioremediation of organic and inorganic contaminants by the process of biodegradation, biosorption, and bioconversion (e.g., Kulshreshtha et al. 2013, 2014; Kumhomkul and Panich-pat 2013; Lamrood and Ralegankar 2013; Ariste et al. 2020; Horel and Schiewer 2020; Esterhuizen et al. 2021).

Fungi are widely investigated for the treatment of wastewater containing organic contaminants such as PAHs and petroleum hydrocarbons (García-Peña et al. 2008; Rene et al. 2012; González-Abradelo et al. 2019; Obire et al. 2020; Li et al. 2021). González-Abradelo et al. (2019) examined two halophilic fungi, *Aspergillus sydowii* and *Aspergillus destruens*, for the removal of PAHs and PhCs at saline conditions. The removal efficiency of benzo(a)pyrene and phenanthrene (PAHs) was above 90%. The authors attributed the removal of both PAHs to biodegradation in the case of *Aspergillus sydowii* and bioadsorption in the case of *Aspergillus destruens*. The removal efficiency of the studied PhCs (ibuprofen and mefenamic acids) was higher than 90% by *Aspergillus sydowii*. Obire et al. (2020) investigated the role of *Aspergillus niger* and *Aspergillus sydowii* in the biodegradation of PAHs in oilfield wastewater. The complete removal of naphthalene and chrysene was observed by *Aspergillus niger*, while *Aspergillus sydowii* showed removal of chrysene only. García-Peña et al. (2008) examined the degradation of BTEX in packed biofilters with the filamentous fungus *Paecilomyces variotii* CBS115145. The results showed the complete degradation of toluene followed by ethylbenzene (90%); however, *meta*-xylene, *para*-xylene, and benzene were partially assimilated (60%, 60%, and 45%, respectively), and *ortho*-xylene was only 30% metabolized in liquid culture after 10 days. The biodegradation and decolorization have been investigated for the treatment of wastewater containing azo dyes (Enayatizamir et al. 2011; De-Miranda et al. 2013; Singh and Singh 2017). Enayatizamir et al. (2011) reported the degradation of black reactive 5 up to 92% by *Phanerochaete chrysosporium* after 3 days of treatment. De-Miranda et al. (2013) reported the decolorization of the effluent containing textile indigo dye up to 95% after 10 days of treatment with *Phanerochaete chrysosporium* URM6181 and *Curvularia lunata* URM6179 strains. Marco-Urrea et al. (2008) examined the potential of white rot fungus *Trametes versicolor* for the biodegradation of chlorinated solvents such as trichloroethylene. The results showed the biodegradation of trichloroethylene (concentration, 2.0 mg/L) up to 88%.

Several studies examined the potential of fungi for the treatment of wastewater containing PhCs, PCPs, and SHs (e.g., Santos et al. 2012; Taştan and Dönmez 2015; Esterhuizen-Londt et al. 2017; Esterhuizen et al. 2021). Esterhuizen-Londt et al. (2017) investigated the uptake and accumulation of PhCs such as diclofenac by the aquatic fungus *Mucor hiemalis*. The cultures of *Mucor hiemalis* were exposed to different concentrations of diclofenac (10, 25, and 50 μg/L) over a period of 144 h. The removal efficiency of diclofenac was 95% within 24 h with all the studied concentrations. However, *Mucor hiemalis* showed the poor removal efficiency of acetaminophen (26%) after 7 days, while *Phanerochaete chrysosporium* showed the high removal efficiency of acetaminophen after 3 and 7 days (97% and 99%, respectively) (Esterhuizen et al. 2021). Santos et al. (2012) evaluated the potential of *Pleurotus* sp. P1, *Pleurotus ostreatus* BS, and basidiomycete strain BNI to degrade SHs such as 17α-ethinylestradiol and PhCs such as carbamazepine individually. The results showed the complete degradation of 17α-ethinylestradiol (both in the absence and presence of another carbon source—glucose), whereas carbamazepine was only degraded with basidiomycete strain BNI in the presence of glucose (47%). Taştan and Dönmez (2015) studied the biodegradation of PCPs such as triclosan by *Aspergillus versicolor*. The results showed the biodegradation of triclosan (concentration, 7.5 mg/L) up to 72%. Fungi are also investigated for the treatment of wastewater containing pesticides (Gaber et al. 2020; Levio-Raiman et al. 2021). Gaber et al. (2020) examined the degradation of diazinon by three fungal species, *Rhizopus nodosus*, *Aspergillus fumigatus*, and *Penicillium citreonigum*, which were isolated from the wastewater. The corresponding removal efficiency of diazinon was 91%, 76%, and 72%, respectively. Levio-Raiman et al. (2021) studied the biodegradation of atrazine, iprodione, and chlorpyrifos by consortium of two fungal strains (*Verticillium* sp. H5 and *Metacordyceps* sp. H12). The corresponding removal efficiency was 59%, 96%, and ~85% within 10 days.

Fungi have been used for bioremediation of PTMs as they exhibit strong resistance to PTM toxicity and were able to take up high metal (Yin et al. 2019; Mal and Rangabhashiyam 2021). The glucuronic acid, phosphate, and chitin-chitosan complex along with different functional groups such as carboxyl, amine, phosphate, hydroxyl, and sulfhydryl groups play a significant role in the biosorption of PTMs and the sorption capability of fungi (Yin et al. 2019; Mal and Rangabhashiyam 2021). Iram et al. (2015) demonstrate biosorption of Pb(II) using *Aspergillus niger* with high biosorption capacities. *Aspergillus fumigatus* isolated from mine drainage showed strong biosorption capability for Cr(VI) with maximum uptake of 48.2 mg/g (Dhal and Pandey 2018). *Saccharomyces cerevisiae* has also been explored for the successful bioremediation of Cd, Cu, and Zn from the wastewater (Yin et al. 2019). *Talaromyces islandicus* and *Aspergillus terreus* isolated from sewage sludge and industrial effluents exhibited higher resistance to lead ions and were able to remove 80% of lead ions (Mal and Rangabhashiyam 2021). The fungal consortia comprising of *Ascomycota* and *Basidiomycota* showed effective removal of As, Cu, Cr, and Mn (Hassan et al. 2020).

Rhizophagus irregularis (previously known as *Glomus intraradices*), an arbuscular mycorrhizal fungus, shows strong biosorption and bioaccumulation of U (Das 2012). *Penicillium* sp. isolated from mining area demonstrated strong resistance to U. *Gongronella* sp. and *Talaromyces* sp. were also used successfully for the bioremediation of U (Coelho et al. 2020). Dhami et al. (1998) demonstrated biosorption of radionuclides including U, Pu, cerium (Ce), and europium (Eu) from aqueous solution using *Rhizopus arrhizus*, *Gibberella fujikuroi*, *G. fujikuroi* NCIM 665, and *G. saubinetti* NCIM 85, among which *R. arrhizus* was the most promising fungi biomass for the bioremediation of radioactive waste from nuclear industry. *Cladosporium cladosporioides* also exhibits strong biosorption capacity and was used successfully for the removal of Cs and Sr (Das 2012).

4.4.1.3 Phycoremediation

The phycoremediation involves the use of micro- or macroalgae for the uptake of a complex pollutant (organic and inorganic) from the wastewater, which utilizes them as source of nutrients or transforms them to nontoxic form (Quintana et al. 2011; Fayyad et al. 2020). Algae are known to remove organic and inorganic contaminants from the wastewater by bioabsorption, bioaccumulation, and biotransformation (Kobayashi and Rittman 1982; Dosnon-Olette et al. 2010; Ji et al. 2011; Priyadarshani et al. 2011; Escapa et al. 2016). For instance, the presence of various surface receptors such as lipid, proteins, and polysaccharides on the outer surface of algae enables pollutants to bind passively by the phenomenon known as bioabsorption (Priyadarshani et al. 2011). However, the uptake of pollutants inside the cell is done through active transport. In case of bioaccumulation, both the passive absorption and active uptake of the pollutant by the algal cell take place. In addition to that, algae can remove organic contaminants by biodegradation, which involves the decomposition of the complex toxic organic contaminants into a simpler non-toxic organic compound such as carbon dioxide and water (Pandey et al. 2019).

Several studies reported the phytoremediation of organic contaminants by biodegradation and biotransformation. For instance, de Llasera et al. (2016) evaluated the comparative performance of two microalgal species, *Selenastrum capricornutum* and *Scenedesmus acutus*, for the removal of PAHs such as benzo(a)pyrene by sorption and degradation. The almost complete removal of benzo(a)pyrene was achieved by *Selenastrum capricornutum* at 15 h of exposure (99%) and *S. acutus* at 72 h of exposure (95%). The authors reported that the removal mechanisms of benzo(a)pyrene in the case of *S. capricornutum* were sorption and biodegradation, whereas, in the case of *S. acutus*, it was sorption rather than biodegradation. The formation of TPs (4,5-dihydrodiol benzo(a)pyrene, 7,8-dihydrodiol benzo(a)pyrene, and 9,10-dihydrodiol benzo(a)pyrene) by *Selenastrum capricornutum* was rapid and proportional to the amount of the benzo(a)pyrene added to cultures compared with *Scenedesmus acutus*. Hong et al. (2008) reported the bioaccumulation and biodegradation of two PAHs, phenanthrene and fluoranthene, by two diatoms sp. *Skeletonema costatum* and *Nitzschia* sp. The authors concluded that a mixture of phenanthrene and fluoranthene showed higher removal efficiency compared with phenanthrene and fluoranthene alone. This indicates that the presence of one type of PAH stimulates the degradation of other. Takáčová et al. (2015) examined the biodegradation of BTEX by microalgae *Parachlorella kessleri*. The authors observed that benzene and xylenes were degraded up to 40% and toluene up to 63% within 48 h, whereas ethylbenzene was degraded only up to 30% after 72 h. Lim et al. (2010) examined *Chlorella vulgaris* for the bioremediation of textile wastewater using four batches of cultures in high-rate algae ponds containing azo dyes supranol red 3BW. The color removal ranged from 42% to 50%. Acuner and Dilek (2004) reported that the color removal of monoazo dye tectilon yellow 2G ranged from 63% to 90% by *Chlorella vulgaris*. Saloglu and Sahin (2021) examined the *Spirulina* microalgae-immobilized alginate beads as adsorbents for the adsorption of azo dyes such as tartrazine, carmoisine, and allura red from the wastewater. The beads showed high adsorption capacities indicated by the high removal efficiency of tartrazine, carmoisine, and allura red (98%, 93%, and 82%, respectively) within 2 h. Smets and Rittmann (1990) studied the sorption of chlorinated solvents such as trichloroethylene with three species of algae including *Chlorella vulgaris*, *Scenedesmus quadricauda*, and *Selenastrum capricornutum*.

Ding et al. (2017) investigated the removal of PhCs such as naproxen with the use of *Cymbella* sp. and *Scenedesmus quadricauda*. The authors reported that both *Cymbella* sp. and *Scenedesmus quadricauda* showed complete growth inhibition (100%) at 100 mg/L within 24 h. The removal efficiency of naproxen was higher (97%) with *Cymbella* sp. spiked with 1.0 mg/L of naproxen compared with *Scenedesmus quadricauda* (59%). Escapa et al. (2015) studied the removal of salicylic acid and acetaminophen from the water by *Chlorella sorokiniana*. The authors observed about 70% removal of both the studied PhCs at the end of the batch. In another study, the authors compared the performance of three different microalgae strains including *Chlorella sorokiniana*, *Chlorella vulgaris*, and *Scenedesmus obliquus* for the removal of diclofenac. The results showed the largest increase of growth rate and microalgae density (25% and 31%, respectively) by *Chlorella sorokiniana*. However, *Scenedesmus obliquus* showed the highest removal efficiency of diclofenac (>79%) (Escapa et al. 2016). Wang et al. (2018) studied the performance of three common freshwater microalgae including *Chlorella pyrenoidosa*, *Desmodesmus* sp., and *Scenedesmus obliquus* for the removal of PCPs such as triclosan from the wastewater. The high removal efficiency (up to 99.7%) of triclosan was observed, and its removal was attributed to cellular uptake by *Chlorella pyrenoidosa* and biotransformation by *Desmodesmus* sp. and *Scenedesmus obliquus*. Hom-Diaz et al. (2015) investigated the performance of microalgae *Selenastrum capricornutum* and *Chlamydomonas reinhardtii* for the removal of SHs such as 17α-ethinylestradiol and 17β-estradiol. The authors reported that the removal efficiency of 17α-ethinylestradiol and 17β-estradiol was ranging from 60% to 95% and from 88% to 100%, respectively, by *Selenastrum capricornutum*. Biodegradation contributed from 20% to 54% and from 42% to 54% of the total removal efficiency, respectively, and the rest of the removal was attributed to adsorption onto the algae biomass. However, *Chlamydomonas reinhardtii* presented higher adsorption of 17α-ethinylestradiol and 17β-estradiol (71% and 86%, respectively). In another study, the performance of microalgae *Desmodesmus* sp. WR1 was tested for the removal of 17β-estradiol from the wastewater. The removal efficiency of 17β-estradiol was ranging from 85% to 99%, and the removal was attributed to biotransformation and biodegradation (Wang et al. 2020). Friesen-Pankratz et al. (2003) reported that the presence of *Selenastrum capricornutum* decreased the aqueous persistence of pesticides such as atrazine. Hussein et al. (2017) reported the removal of several pesticides including atrazine, molinate, simazine, isoproturon, propanil, carbofuran, dimethoate, pendimethalin, metolachlor, and pyriproxin by biosorption onto *Chlorella vulgaris* using short- and long-term exposures. In the short-term study, the removal of pesticides ranged from 86% to 89% in the presence of living cells and ranged from 96% to 99% in the presence of lyophilized algal biomass. However, in the long-term study, the removal of pesticides ranged from 87% to 96.5% in the presence of growing algae.

Microalgae are also known as highly efficient biosorbent for the removal of PTMs via biosorption (Zeraatkar et al. 2016; Yin et al. 2019; Mal and Rangabhashiyam 2021). Initially PTM ions interact with various peptides excreted by algae as part of biosorption mechanisms which also protect the algae from PTM toxicity (Bilal et al. 2018). *Durvillaea antarctica* showed strong biosorption of Cu via interaction between Cu ions and hydroxyl groups present on the cell wall (Cid et al. 2015). Rangabhashiyam et al. (2016) explored *Enteromorpha* sp., and the maximum biosorption and removal of Cr(VI) were reported at pH 2.0. The strong adsorption properties of *Fucus vesiculosus* (Demey et al. 2018) and *Cladophora fascicularis* (Deng et al. 2007) were explored for the biosorption and removal of Pb (II), which comply with Langmuir and Freundlich isotherm models. PTMs' removal from a multi-metallic solutions comprising of As, Cu, Mn, and Zn using *Scenedesmus almeriensis* and *Chlorella vulgaris* was demonstrated by Saavedra et al. (2019). *Scenedesmus obliquus* was able to remove 93% of Cd of the initial Cd concentration of 50 mg/L in the acidic conditions and also showed strong biosorption capacity during the entire five recycles (Mal and Rangabhashiyam 2021). *Desmodesmus* sp. and *Heterochlorella* sp. are the two acid-tolerant microalgae known for the simultaneous removal of Fe, Zn, and Mn at pH 3.5 via intracellular accumulation mechanisms (Abinandan et al. 2019). Non-living biomass of *Sargassum fluitans*, brown algae, was explored for the sorption of U from aqueous solution (Yang and Volesky 1999). Aleissa et al. (2004) demonstrated uptake and removal of U by filamentous green algae such as *Spirogyra* and *Cladophora* spp.

4.4.1.4 Phytoremediation

Phytoremediation technology involves the utilization of plants and the associated rhizosphere microorganisms to degrade, remove, or transform the pollutants located in soils, sediments, and ground and surface water (Susarla et al. 2002; Carvalho et al. 2014; Muthusaravanan et al. 2018; Palansooriya et al. 2020; Antoniadis et al. 2021). Phytoremediation techniques can be classified as phytoextraction, phytotransformation, phytostabilization, phytodegradation, rhizofiltration, and phytovolatilization based on the fate of contaminants in the vegetation-based remediation (Vidali 2001). For instance, in phytoremediation, contaminants can be transported across plant membranes from the soil or water, and the ones with low molecular weight are easily taken up by the plants and released through leaves by evapotranspiration process (phytovolatilization). Nevertheless, the non-volatile compounds can be degraded or converted into nontoxic compounds by enzymatic modification and sequestration in the plants (phytodegradation and phytoextraction). On the other hand, some compounds are stable in the plants (phytostabilization). These compounds can be removed along with the biomass for incineration or sequestration (Gerhardt et al. 2009; Carvalho et al. 2014; Muthusaravanan et al. 2018; Jain et al. 2020; Antoniadis et al. 2021).

Various plant species including *Brassica napus*, *Helianthus annuus*, *Jatropha curcas*, *Pisum sativum*, *Puccinellia frigida*, *Pteris vittata*, *Ricinus communis*, and *Stanleya pinnata* have been widely reported for the phytoextraction of PTMs (Yadav et al. 2018; Patra et al. 2020; Mal and Rangabhashiyam 2021). All these plant species have shown greater capacity to take up and accumulate PTMs with high tolerance to PTM toxicity. The phytostabilization has been reported for the remediation of various toxic metals such as As, Cd, Cu, Cr, Zn, and Pb from the contaminated site using different plant species including *Agrostis* spp., *Brassica juncea*, *Epilobium dodonaei*, *Festuca* spp., *Hordeum vulgare*, *Iris sibirica*, *Lupinus luteus*, and *Vicia villosa* (Yadav et al. 2018; Mal and Rangabhashiyam 2021). However, phytodegradation is mainly limited to organic contaminant as PTMs are nonbiodegradable. Nevertheless, few toxic metal(loid)s like Hg and Se can be biomethylated to less toxic volatile form, i.e., mercuric oxide/elemental Hg and dimethyl selenide, respectively, which eventually escape into the atmosphere (Wang et al. 2012; Dhillon and Bañuelos 2017; Yadav et al. 2018; Patra et al. 2020). For example, Pilon-Smits and Pilon (2000) demonstrated high volatilization of toxic Hg (II) and methyl mercury into a less toxic elemental mercury using genetically modified *Arabidopsis thaliana* and *Nicotiana tabacum. Pteris vittata* was demonstrated for the volatilization of As into the atmosphere from the contaminated site (Sakakibara et al. 2010).

In the following section, the removal of organic and inorganic contaminants from the wastewater is discussed in detail with the application of constructed wetlands (CWs), which is a phytoremediation technology.

4.5 Constructed Wetlands

CWs involve the growth of macrophytes in a pond and the use of sunlight to produce oxygen, which is used by microorganisms to degrade organic matter in the wastewater. This interaction of plants, microorganisms, and soil leads to natural processes (physical, chemical, and biological), which are used to remove pollutants (organic and inorganic) from the wastewater (Vymazal 2005; Kadlec and Wallace 2009; Hale et al. 2021) (Fig. 4.10).

4.5.1 Design and Types of CWs

Traditionally, CWs have been designed as free water surface CW (FWSCW) and subsurface flow CW (SSFCW). The SSFCW are further categorized into horizontal subsurface flow CW (HFCW) and vertical subsurface flow CW (VFCW). Brief information on CW types is presented here, and detailed description can be found in the literature (e.g., Vymazal 2005; Kadlec and Wallace 2009; Ilyas and Masih 2017a, b). FWSCW consists of open water, floating vegetation, and emergent plants.

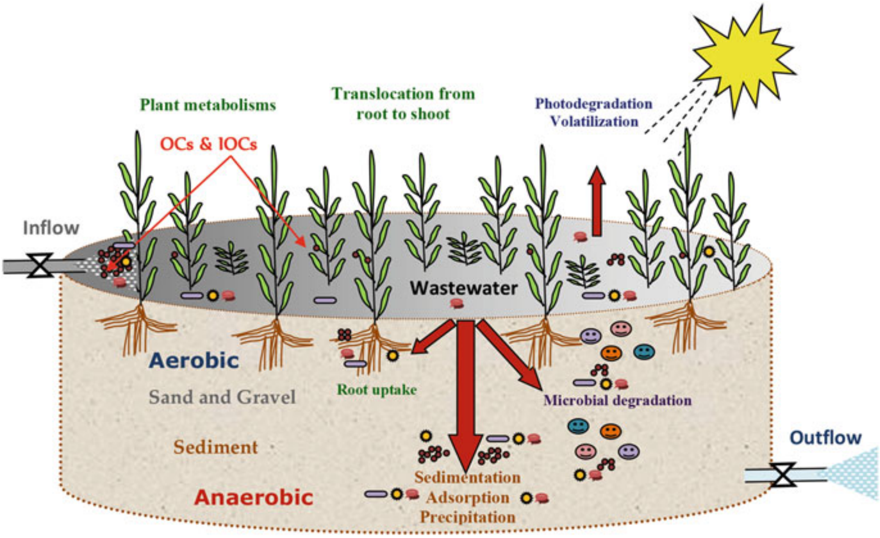


Fig. 4.10 A schematic representation of the removal mechanisms of organic and inorganic contaminants in SSFCW. *OCs* organic compounds, *IOCs* inorganic compounds

In HFCW, wastewater stays below the surface of the media and flows horizontally through the bed until it reaches the outlet. In VFCW, the beds are pulse-loaded with a large amount of water to temporarily flood the surface of the bed (Kadlec and Wallace 2009). Due to the limitations and different removal mechanisms in different types of CWs, a hybrid CW (HCW) is designed to achieve the higher performance compared with only one setting of a CW. For example, HCW consisting of VFCW and HFCW was developed to enhance the removal of nitrogen by providing nitrification-denitrification processes (Cooper et al. 1999; Kadlec and Wallace 2009; Vymazal 2013). Later, the other types of HCW were investigated and developed such as FWSCW combined with VFCW and/or HFCW to enhance the performance of CWs for the removal of organic and inorganic pollutants, which require several processes for their removal (e.g., Vymazal 2013; Ávila et al. 2014a; Kahl et al. 2017; Nivala et al. 2019; Ilyas and van Hullebusch 2020a, b, c). Moreover, several individual studies examined the effect of plants in CWs by considering the removal of organic and inorganic pollutants in the planted and unplanted CWs (Dan et al. 2013; Button et al. 2019; Campos et al. 2019; Ilyas and van Hullebusch 2019, 2020b, d). The role of a support matrix of CWs in the removal of organic and inorganic pollutants was explored by several authors, by using a substrate material of high adsorption capacity, rich in organic surfaces, and with high surface area (Chen et al. 2016; Xie et al. 2018; Ilyas and van Hullebusch 2019, 2020b, d; Nivala et al. 2019).

4.5.2 Removal Mechanisms of Organic and Inorganic Contaminants in CWs

CWs have been extensively investigated for the removal of organic contaminants (priority substances and EOCs) and inorganic contaminants from the wastewater and groundwater such as PAHs (Poerschmann and Schultze-Nobre 2014; Zhao et al. 2021), petroleum hydrocarbons (Ranieri et al. 2013; Mustafa et al. 2018; Abdullah et al. 2020; Jain et al. 2020; Stefanakis 2020), azo dyes (Saeed and Sun 2017; Hussein and Scholz 2018; Kumar et al. 2018), chlorinated solvents (Field and Sierra-Alvarez 2004; Chen et al. 2012, 2017a; Al-Baldawi et al. 2015; Al-Baldawi 2018), PhCs (Zhang et al. 2014; Gorito et al. 2017; Ilyas et al. 2020), PCPs (Verlicchi et al. 2015; Vo et al. 2018; Ilyas and van Hullebusch 2020a), SHs (Töre et al. 2012; Vymazal et al. 2015; Ilyas and van Hullebusch 2020b), pesticides (Vymazal and Březinová 2015; Lv et al. 2016; Tournebize et al. 2017; Lyu et al. 2018; Gikas et al. 2018), nutrients (Vymazal 2007; Kadlec 2016; Ilyas and Masih 2017a, 2018), metal (loid)s (Sheoran and Sheoran 2006; Marchand et al. 2010; Guittonny-Philippe et al. 2014; Sultana et al. 2014; Zhao et al. 2020), and radionuclides (Moogouei and Chen 2020). A large number of studies have been conducted to examine the efficacy and reliability of CWs for the removal of different categories of organic pollutants. Among the investigated CWs were the FWSCW, HFCW, VFCW, and HCW (e.g., Ilyas and van Hullebusch 2020a, b, c).

CWs have shown a potential for the removal of organic contaminants (priority substances and EOCs). Several elimination pathways may occur in a complex CW system: physical processes such as volatilization, sedimentation, and adsorption/sorption; chemical processes such as oxidation, reduction, and photolysis (FWSCW); and biological processes such as microbial degradation, rhizofiltration, and phytoremediation (Kadlec 1992; Suárez et al. 2008; Jain et al. 2020; Hale et al. 2021). However, some processes such as plant uptake and phytovolatilization, contaminant accumulation, and metabolic transformation may be relevant for some plants and organic chemicals (Susarla et al. 2002; Carvalho et al. 2014).

The physicochemical properties of organic compounds and environmental conditions of CWs play a pivotal role in their removal processes. The physicochemical properties of organic compounds, which play a considerable role in the removal processes, are governed by molecular weight/structure, water solubility, octanol-water partition coefficient (Log *Kow*), octanol-water distribution coefficient (Log *Dow*), soil organic carbon sorption coefficient (Log *Koc*), dissociation constant (p*Ka*), cationic or anionic nature (charge), and presence of certain elements (e.g., chlorine well known for its recalcitrance against biodegradation) (Ilyas and van Hullebusch 2020a, b; Ilyas et al. 2020, 2021; Jain et al. 2020; Lee et al. 2020; Khalid et al. 2021; Overdahl et al. 2021). Additionally, it is important to note that certain types of CWs (e.g., FWSCW, HFCW, and VFCW) provide certain environmental conditions to facilitate the specific mechanisms to take place (Ilyas and van Hullebusch 2020a, b, c). For instance, in FWSCW, the main removal mechanism of organic compounds is photodegradation, while microbial degradation and plant uptake also contribute to some extent to their removal. In HFCW and VFCW, the important removal mechanism of organic compounds is anaerobic and aerobic biodegradation, respectively, besides their removal by the filter media (through sedimentation, adsorption, and precipitation) and plant uptake (Table 4.3).

Despite the good performance of CWs, one of their main limitations is that they typically require low hydraulic loading rate (HLR) and therefore require large land area per population equivalent (PE). In order to exploit different degradation pathways (e.g., reductive and oxidative processes) and different environments (e.g., aerobic and anaerobic) to improve the overall effluent water quality, CWs of different configuration can be operated in series, and therefore, they can work at greater HLR (Armenante et al. 1992; Master et al. 2002; Vymazal 2005). Thus, the researchers have started looking into combinations of different types of CWs, the so-called HCW, for the enhanced removal of organic contaminants and their TPs (Masi et al. 2004; Conkle et al. 2008; Reyes-Contreras et al. 2012; Ávila et al. 2014a, 2015; Dai et al. 2017; Sgroi et al. 2018).

4.5.3 Performance of CWs for Organic Contaminants' Removal

4.5.3.1 Polycyclic Aromatic Hydrocarbons

Several studies investigated the performance of different types of CWs (FWSCW, HFCW, VFCW, and HCW) for the treatment of wastewater containing PAHs (Wojciechowska 2013; Leung et al. 2016; Yi et al. 2016; Walaszek et al. 2018; Kang et al. 2019; Alsghayer et al. 2020; Nas et al. 2020; Zhao et al. 2021). Kang et al. (2019) explored the performance of FWSCW (planted with *Oenanthe javanica*) for the treatment of wastewater containing three-ring PAHs (acenaphthene, acenaphthylene, and fluorene) and four-ring PAHs (fluoranthene and pyrene). The removal efficiency of three-ring and four-ring PAHs in FWSCW was 99.8% and 88%, respectively. Yi et al. (2016) studied the performance of HFCW for the treatment of industrial wastewater containing phenanthrene. The results showed the high removal efficiency of phenanthrene (92%). Alsghayer et al. (2020) examined the performance of HFCWs planted with *Phragmites* and *vetiver* for the treatment of industrial wastewater containing phenanthrene, pyrene, and benzo(a)pyrene. The corresponding removal efficiency of the studied PAHs in HFCW planted with *Phragmites* (83%, 71%, and 81%, respectively) was higher compared with HFCW planted with vetiver (67%, 66%, and 73%, respectively) and unplanted CW (62%, 58%, and 55%, respectively). The comparatively better removal efficiency in the planted CW compared with unplanted CWs indicated the role of plants in removing PAHs from the wastewater. Leung et al. (2016) examined the effectiveness of VFCW (using dominant mangrove plants, *Aegiceras corniculatum* and *Bruguiera gymnorrhiza*, and common wetland plants, *Acorus calamus*, *Canna indica*, and *Phragmites australis*, in different cultural arrangements (mono- and mixed cultures)) to treat wastewater containing phenanthrene, pyrene, and benzo(a)pyrene. All the studied PAHs were almost completely removed (above 99%) by the VFCWs planted with mangrove and non-mangrove, irrespective of planting arrangement. Wojciechowska (2013) investigated the performance of

Table 4.3 The major removal mechanisms of organic and inorganic contaminants in CWs

Category of contaminants	Major removal mechanisms in CWs	References
Organic contaminants		
Polycyclic aromatic hydrocarbons	• Biodegradation • Adsorption • Sorption • Phytoextraction/plant uptake • Phytovolatilization	Wojciechowska (2013), Poerschmann and Schultze-Nobre (2014), Leung et al. (2016), Kang et al. (2019), Alsghayer et al. (2020), Zhao et al. (2021)
Petroleum hydrocarbons	• Phytovolatilization • Phytoextraction/plant uptake • Biodegradation (aerobic)	Ranieri et al. (2013), Mustafa et al. (2018), Abdullah et al. (2020), Jain et al. (2020), Stefanakis (2020)
Azo dyes	• Biodegradation (aerobic and anaerobic) • Rhizoremediation	Davies et al. (2006), Ong et al. (2011), Saeed and Sun (2017), Skrzypiec and Gajewska (2017), Hussein and Scholz (2018), Kumar et al. (2018)
Chlorinated solvents	• Biodegradation (aerobic and/or anaerobic)	Field and Sierra-Alvarez (2004), Chen et al. (2012, 2017a), Al-Baldawi et al. (2015), Al-Baldawi (2018)
Pharmaceuticals	• Biodegradation (aerobic and/or anaerobic) • Adsorption to the substrate • Plant uptake • Photodegradation	Chen et al. (2016), Petrie et al. (2018), Zhang et al. (2018b), Ilyas and van Hullebusch (2019, 2020c), Ilyas et al. (2020)
Personal care products	• Adsorption to the substrate and/or sorption onto organic/ inorganic surfaces • Biodegradation (aerobic and/or anaerobic) • Plant uptake	Ávila et al. (2014a, b), Hijosa-Valsero et al. (2016), Matamoros et al. (2016, 2017), Vymazal et al. (2017), Ilyas and van Hullebusch (2020a)
Steroidal hormones	• Biodegradation (aerobic and/or anaerobic) • Plant uptake • Adsorption to the substrate and/or sorption onto organic surfaces	Vymazal et al. (2015), Herrera-Melián et al. (2018), Chen et al. (2019), Ilyas and van Hullebusch (2020b)
Pesticides	• Biodegradation (aerobic) • Plant uptake • Adsorption to the substrate • Photodegradation • Hydrolysis	Vymazal and Březinová (2015), Lv et al. (2016), Chen et al. (2017b), Tournebize et al. (2017), Lyu et al. (2018)
Inorganic contaminants		
Metal(loid)s and radionuclides	• Adsorption and/or biosorption • Hydrolysis • Sedimentation and/or precipitation • Oxidation and/or reduction • Plant uptake	Sobolewski (1999), Kosolapov et al. (2004), Sheoran and Sheoran (2006), Dorman et al. (2009), Marchand et al. (2010), Vymazal and Březinová (2016), Sochacki et al. (2018), Batool and Saleh (2020), Zhao et al. (2020), Moogouei and Chen (2020)

FWSCW, HFCW, and HCW (combination of two VFCWs followed by HFCW) for the treatment of landfill leachate containing fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)-fluoranthene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)-perylene, and dibenzoanthracene. The total removal efficiency of the studied PAHs was higher in HCW (94%) compared with HFCW (63%). However, in FWSCW, the total outflow concentration of PAHs was higher than their inflow concentration (4.63 μg/L and 2.99 μg/L, respectively). The author attributed this negative removal to resuspension or desorption of PAHs deposited in the sediments. The major removal mechanisms of PAHs in CWs are biodegradation, adsorption and/or sorption, phytoextraction/plant uptake, and phytovolatilization (Table 4.3).

4.5.3.2 Petroleum Hydrocarbons

Several studies explored the performance of different types of CWs for the treatment of wastewater containing petroleum hydrocarbons (Ranieri et al. 2013; Mustafa et al. 2018; Abdullah et al. 2020; Jain et al. 2020; Stefanakis 2020). Ranieri et al. (2013) examined the performance of different configurations of HFCW (planted, *Phragmites australis* and *Typha latifolia*, and unplanted). The removal efficiency of BTEX ranged from 46% to 55%. The average removal efficiency was 5% higher in HFCW planted with *Phragmites australis* compared with *Typha latifolia* field and 23% higher compared with the unplanted HFCW. Mustafa et al. (2018) investigated the performance of FWSCW for the treatment of wastewater containing BTEX. The influent concentration of benzene, toluene, ethylbenzene, *meta*-xylene, *para*-xylene, and *ortho*-xylene was 1.57 mg/L, 0.14 mg/L, 0.29 mg/L, 2.01 mg/L, 2.01 mg/L, and 0.13 mg/L, respectively. The results showed the high performance of FWSCW for the removal of BTEX. The removal efficiency of benzene, toluene, ethylbenzene, *meta*-xylene, *para*-xylene, and *ortho*-xylene was 93%, 93%, 98%, 91%, 91%, and 87%, respectively. To date, the performance of all types of CWs is not investigated for the removal of BTEX from the wastewater (e.g., Stefanakis 2020). Stefanakis (2020) examined the performance of different types of CWs (FWSCW, HFCW, VFCW, and HCW) for the removal of benzene from the wastewater. The analysis revealed that VFCW performed better for the removal of benzene compared with other types of CWs considering the availability of better aeration conditions in VFCW required for the biodegradation of benzene. The major removal mechanisms of BTEX were phytovolatilization, phytoextraction/plant uptake, and biodegradation (aerobic) (Table 4.3).

4.5.3.3 Azo Dyes

The performance of different types of CWs (e.g., HFCW, VFCW, and HCW) is investigated for the treatment of wastewater containing azo dyes (Davies et al. 2006; Bulc and Ojstršek 2008; Ong et al. 2011; Saeed and Sun 2013; Tee et al. 2015; Hussein and Scholz 2018). Bulc and Ojstršek (2008) examined the performance of a HCW (combination of two parallel VFCWs followed by a HFCW) for the treatment of dye-rich textile wastewater with the special focus on color reduction. The results showed a good performance of the system for the removal efficiency of chemical oxygen demand (COD) (84%), total organic carbon (TOC) (89%), and color (90%). Saeed and Sun (2013) studied the performance of HCW (combination of VFCW and HFCW) for the treatment of textile wastewater. The color removal efficiency was higher in the HFCW (ranging from 61% to 79%) compared with VFCW (ranging from 37% to 61%) indicating that color removal processes were prominent under anaerobic conditions. However, the overall color removal efficiency was ranging from 76% to 91% (at 500–800 nm wavelengths), which was comparable with the color removal efficiency achieved by the HCW of Bulc and Ojstršek (2008). Davies et al. (2006) investigated the performance of VFCW for the removal of acid orange 7 from the wastewater. The results showed the high color removal efficiency (99%) demonstrating the cleavage of azo bonds as well as high COD and TOC removal efficiency (93%) indicating biodegradation of acid orange 7. Although these studies reported a good color removal efficiency, the degradation route of dyes and subsequent byproduct formation (due to anaerobic dye degradation) was not studied, which was investigated by Ong et al. (2011). The authors examined the performance of a laboratory-scale VFCW under aerated (artificial aeration (AA)) and non-aerated (NA) conditions for the removal of acid orange 7 from the wastewater. The results showed the high removal efficiency of acid orange 7 (above 94%) under both conditions; however, the AA-VFCW performed better than the NA-VFCW for the removal of COD (95% and 62%, respectively) and aromatic amines generated from the reduction of azo dye. Hussein and Scholz (2018) investigated the performance of VFCW for the removal of acid blue 113 and basic red 46. The removal efficiency of the studied azo dyes and a mixture dye of both of them was ranging from 85% to 100%. Tee et al. (2015) developed HFCW incorporating baffles to facilitate upflow and downflow conditions in order to treat the pollutants under aerobic, anoxic, and anaerobic conditions sequentially in the same CW. The performances of the baffled HFCW and conventional HFCW (planted and unplanted) were investigated for the treatment of domestic wastewater spiked with acid orange 7 (concentration, 300 mg/L) at hydraulic retention time (HRT) of 5, 3, and 2 days. The corresponding removal efficiency of acid orange 7 in planted baffled HFCW was higher (100%, 83%, and 69%, respectively) compared with conventional HFCW (73%, 46%, and 30%, respectively). The complete biodegradation of acid orange 7 in planted baffled HFCW was attributed to the availability of a combination of aerobic, anoxic, and anaerobic conditions. The major removal mechanisms of azo dyes in CWs are biodegradation (aerobic and anaerobic) and rhizoremediation (Table 4.3).

4.5.3.4 Chlorinated Solvents

Chlorinated solvents are among the most common organic contaminants of wastewater and groundwater. Among the CWs, HFCW are investigated for the treatment of wastewater (Chen et al. 2017a; Al-Baldawi 2018) and groundwater (Bankston et al. 2002; Chen et al. 2012; Al-Baldawi et al. 2015) containing chlorinated solvents. Chen et al. (2017a) examined the performance of pilot-scale HFCW to treat wastewater containing chlorinated solvents such as tetrachloroethylene (perchloroethylene) with three different flow regimes (continuous flow, 7-day cycle discontinuous flow, and 2.5-day cycle discontinuous flow). The results showed that intensifying the tidal regime (2.5-day cycle) enhanced the removal efficiency of tetrachloroethylene at 0.5 m by promoting its dechlorination process and formation of *cis*-1,2-dichloroethylene, vinyl chloride, and ethene. Al-Baldawi (2018) studied the performance of pilot-scale HFCW to treat industrial wastewater containing 1,2-dichloroethane. Three HFCWs (HFCW 1, unplanted and contained sand acting as contaminant control; HFCW 2, planted and contained sand; and HFCW 3, planted and contained mixture of sand, soil, and compost (3:2:1)) were fed with wastewater, and one HFCW was fed with tap water (control) to assess the role of *Typha angustifolia* L. and their associated rhizobacteria to remediate 1,2-dichloroethane. The results showed the higher removal efficiency of 1,2-dichloroethane (100%) by HFCW 3 (planted and contained mixture of sand, soil, and compost) compared with HFCW 2 and HFCW 1 (planted and unplanted and contained sand) (82% and 57%, respectively). Chen et al. (2012) examined two pilot-scale HFCWs (planted and unplanted) for the treatment of groundwater containing tetrachloroethylene (perchloroethylene) (2.0 mg/L). The results showed the almost complete removal of tetrachloroethylene in both HFCW, and up to 70% and 25% of tetrachloroethylene was dechlorinated to *cis*-1,2-dichloroethylene and vinyl chloride after 4 m from the inlet, respectively. The major removal mechanism of chlorinated solvents in CWs is biodegradation (aerobic and anaerobic) (Table 4.3).

4.5.3.5 Pharmaceuticals

Zhang et al. (2018b) investigated the performance of three types of planted and unplanted CWs (FWSCW, HFCW, and VFCW) for the treatment of wastewater containing PhCs including ibuprofen, gemfibrozil, naproxen, ketoprofen, and diclofenac. The results indicated the high variability in the removal efficiency of PhCs in different types of CWs (FWSCW, ranging from 10% to 90%; HFCW, ranging from 40% to 82%; and VFCW, ranging from 38% to 75%). HFCW and VFCW showed the high removal efficiency for ibuprofen (80% and 62%, respectively), gemfibrozil (70% and 58%, respectively), and naproxen (82% and 75%, respectively), whereas FWSCW performed better for ketoprofen (90%) and diclofenac (68%). Ilyas et al. (2020) presented a comprehensive and critical analysis regarding the removal of PhCs, the governing physicochemical properties, and the removal mechanisms in CWs. Despite large variability, CWs have demonstrated their capability to effectively and efficiently remove a large number of PhCs from the wastewater (e.g., 96 out of 113 compounds or 85% of the sample showed a positive removal efficiency). The average removal efficiency of 33 out of 34 widely studied PhCs (diclofenac, ibuprofen, ketoprofen, naproxen, salicylic acid, acetaminophen, codeine, tramadol, clarithromycin, doxycycline, erythromycin, ofloxacin, oxytetracycline, sulfadiazine, sulfamethazine, sulfamethoxazole, sulfapyridine, trimethoprim, monensin, fexofenadine, caffeine, diltiazem, carbamazepine, mirtazapine, venlafaxine, atenolol, metoprolol, sotalol, ranitidine, bezafibrate, clofibric acid, gemfibrozil, and furosemide) ranged from 21% to 93%, with an exception of lincomycin that exhibited a negative removal efficiency (on average), though with very high standard deviation (−441 ± 1001%). A comparative analysis of the removal efficiency of 29 selected PhCs (diclofenac, ibuprofen, ketoprofen, naproxen, salicylic acid, acetaminophen, codeine, tramadol, clarithromycin, doxycycline, ofloxacin, sulfadiazine, sulfamethazine, sulfamethoxazole, sulfapyridine, trimethoprim, fexofenadine, caffeine, diltiazem, carbamazepine, mirtazapine, venlafaxine, atenolol, metoprolol, sotalol, ranitidine, bezafibrate, clofibric acid, and gemfibrozil) by different types of CWs (FWSCW, HFCW, VFCW, and HCW) was conducted by Ilyas and van Hullebusch (2020c). The removal efficiency of 12 out of 29 selected PhCs (diclofenac, ibuprofen, naproxen, tramadol, sulfapyridine, trimethoprim, caffeine, mirtazapine, venlafaxine, ranitidine, clofibric acid, and gemfibrozil) revealed significant differences in different types of CWs. Although all types of studied CWs have demonstrated a good capacity for removing a variety of PhCs, HCW performed better followed by VFCW, HFCW, and FWSCW for most of the 29 selected PhCs. The major removal mechanisms for most of the examined PhCs in CWs are biodegradation (aerobic and/or anaerobic), adsorption to the substrate and/or sorption onto organic/inorganic surfaces, plant uptake (planted CWs), and photodegradation (FWSCW) (Table 4.3).

4.5.3.6 Personal Care Products

Ávila et al. (2015) examined the treatment performance of a full-scale HCW (combination of VFCW, HFCW, and FWSCW connected in series) for the removal of PCPs such as tonalide and triclosan from primary treated combined sewer effluent (i.e., domestic wastewater together with the urban runoff). The removal efficiency of tonalide and triclosan was 94% and 77%, respectively, at HLR of 0.04 m^3/m^2/day and organic loading rate (OLR) of 11 g COD/m^2/day with corresponding HRT of 7.4 days. Sgroi et al. (2018) studied the performance of VFCW and HCW (combination of VFCW, HFCW, and FWSCW connected in series) for the treatment of primary effluent containing PCPs such as *N*,*N*-diethyl-meta-toluamide and sucralose. The removal efficiency of *N*,*N*-diethyl-meta-toluamide and sucralose was 28% and 4.4%, respectively, in VFCW at HLR of 0.1 m^3/m^2/day and OLR of 11 g COD/m^2/day. Although sucralose was not removed under these operational conditions in HCW, *N*,*N*-diethyl-meta-toluamide showed 80% removal efficiency. Ilyas and van Hullebusch (2020a) investigated the performance of different types of CWs (FWSCW, HFCW, VFCW, and HCW) for the removal of PCPs. The 15 widely studied PCPs (acesulfame, methylparaben, propylparaben, *N*,*N*-diethyl-meta-toluamide, triclosan, triclocarban, methyl dihydrojasmonate, cashmeran, galaxolide, tonalide, tributyl phosphate, triphenyl phosphate, tris(2-chloroethyl) phosphate, oxybenzone, and sulisobenzone) showed a positive removal efficiency ranging from 9.0% to 84%. Nevertheless, the six selected PCPs (methylparaben, methyl dihydrojasmonate, triclosan, tonalide, galaxolide, and oxybenzone), which were studied by two or more than two types of CWs, demonstrated a moderate to high removal efficiency ranging from 59% to 84% with the exception of methylparaben (46%). The removal efficiency of three out of six selected PCPs (methylparaben, triclosan, and tonalide) showed significant differences in different types of CWs. Among the studied CWs, the HCW performed better for most of the examined PCPs followed by VFCW, HFCW, and FWSCW. The major removal mechanisms for most of the examined PCPs are adsorption to the substrate and/or sorption onto organic/inorganic surfaces, biodegradation (aerobic and/or anaerobic), and plant uptake (Table 4.3).

4.5.3.7 Steroidal Hormones

Herrera-Melián et al. (2018) examined the performance of HFCW and VFCW for the treatment of wastewater containing SHs including three estrogens (17β-estradiol, estrone, and estriol), two androgens (boldenone and testosterone), three progestogens (levonorgestrel, progesterone, and norethisterone), and one glucocorticoid (prednisone). VFCW performed better than HFCW for the removal of 17-β-estradiol (50% and 30%, respectively), estrone (85% and 63%, respectively), estriol (100% both), testosterone (73% and 45%, respectively), boldenone (100% and −77%, respectively), and progesterone (99% and 84%, respectively). Ilyas and van Hullebusch (2020b) explored the occurrence, fate, and removal of SHs during treatment with different types of CWs (FWSCW, HFCW, VFCW, and HCW). The CWs have demonstrated a good capacity for removing most of the examined SHs from the wastewater. The 11 widely studied SHs (17α-ethinylestradiol, 17-β-estradiol, estrone, estriol, progesterone, norethisterone, levonorgestrel, androstenedione, boldenone, testosterone, and prednisone) showed positive removal efficiency ranging from 55% to 100%. The six selected SHs (17α-ethinylestradiol, 17β-estradiol, estrone, estriol, progesterone, and testosterone), which were studied by two or more than two types of CWs, revealed a moderate to high removal efficiency ranging from 55% to 95%. The removal efficiency of five out of six selected SHs (17α-ethinylestradiol, 17β-estradiol, estrone, estriol, and progesterone) showed significant differences in different types of CWs. Among the studied CWs, the VFCW performed better for most of the examined SHs followed HFCW, HCW, and FWSCW. The major removal mechanisms for most of the examined SHs in CWs are biodegradation (aerobic and/or anaerobic), plant uptake, and adsorption to the substrate and/or sorption onto organic surfaces (Table 4.3).

4.5.3.8 Pesticides

Vymazal and Březinová (2015) presented a comprehensive and critical review of the literature regarding the performance of CWs for removing different categories of pesticides. Despite variable removal efficiency, the CWs revealed the highest removal of some categories of pesticides such as organochlorine (endosulfan and pentachlorophenol, 97%), strobilurin (kresoxim-methyl, trifloxystrobin, and azoxystrobin, 96%), organophosphate (azinphos-methyl, diazinon, dimethoate, glufosinate, chlorpyrifos, methyl parathion, mevinphos, omethoate, parathion, and prothiofos, 94%), and pyrethroids (bifenthrin, cyhalothrin, cypermethrin, esfenvalerate, and permethrin, 84%). On the other hand, the lowest removal was observed for some categories of pesticides such as triazinone (metamitron and metribuzin, 24%), aryloxyalkanoic acid (dichlorprop, 2-methyl-4-chlorophenoxyacetic acid, and mecoprop, 35%), and urea-based pesticide (diuron, fluometuron, chlorotoluron, isoproturon, and linuron, 50%). Chen et al. (2017b) investigated the performance of three types of mesocosm CWs (hydroponic system, FWSCW, and HFCW) for the removal of four herbicides including acetochlor, *s*-

metolachlor, metazachlor, and dimethachlor (concentration, 75 μg/L, 260 μg/L, 1100 μg/L, and 19 μg/L, respectively; air temperature, 20–35 °C). The high removal efficiency (above 92%) of all the four herbicides was observed after 9 days. The major removal mechanisms of pesticides are biodegradation (aerobic), plant uptake, adsorption to the substrate, photodegradation, and hydrolysis (Table 4.3).

4.5.4 Performance of CWs for Inorganic Contaminants' Removal

Metal(loid) removal in CWs is a complex process as various physical, biological, and chemical processes are involved in it including plant uptake and abiotic and biotic reaction (adsorption or biosorption, flocculation, sedimentation and/or precipitation, oxidation or reduction, and plant uptake) (Marchand et al. 2010; Sochacki et al. 2018; Batool and Saleh 2020). In the early stage of CW operation, metal removal largely depends on metal sorption which includes physisorption (i.e., weaker binding via cation exchange) or chemisorption (stronger binding via chemical process) (Sheoran and Sheoran 2006; Marchand et al. 2010; Batool and Saleh 2020). Metals have strong affinity toward organic matter present in the CWs due to plant extracts and shown greater retention via the metal adsorption mechanisms (Sobolewski 1999; Batool and Saleh 2020). A few metals such as Al, Fe, and Mn can precipitate as insoluble compounds as oxides, oxyhydroxides, and hydroxides via hydrolysis and/or oxidation (abiotic or biotic) (Sobolewski 1999; Sheoran and Sheoran 2006; Wu et al. 2019). Fe and Mn oxides in the CWs work as an excellent metal scavenger as they have strong affinity for various metals including Zn, Cu, Cd, Ni, and Pb (Kadlec and Wallace 2009; Sochacki et al. 2018). Fe(III) can deposit onto the roots of plants and form an Fe plaque which becomes a highly effective sink with a large capacity to adsorb the metals (Weiss et al. 2003; Cambrolle et al. 2008). Fe (II) can also co-precipitate with other metals including Cu, Cd, Ni, and Zn as insoluble oxides (Dorman et al. 2009; Sochacki et al. 2018). However, under reducing conditions, this will lead to significant release of metal ions as metals bound/trapped to Fe and Mn oxides will be remobilized into the water via reduction of Fe and Mn oxides in CWs (Goulet and Pick 2001; Sochacki et al. 2018). Various studies demonstrated the importance of plants in CWs for the removal of metals by comparing unplanted and planted CW settings (Khan et al. 2009; Marchand et al. 2010; Batool and Saleh 2020) (Table 4.4). Majority of the metals are removed by the macrophytes during the growth of the plants in the CWs depending on the bioavailability of the metals (Vymazal and Březinová 2016). As plants play an important role in metal removal in CWs, selecting plant species is an important step for better efficiency and continuity of the CW operation (Batool and Saleh 2020). Plants that have fast growth rate, high biomass, and higher metal accumulation capability and are readily available are preferable (Mal and Rangabhashiyam 2021). Plants release various organic acids including acetate, citrate, malonate, and oxalate as root exudates, which can act as chelators for metallic ions and help in phytostabilization of metals in CWs (Ryan et al. 2001). Plants also excrete other organic ligands

Table 4.4 Metal(loid) removal in CWs using different plant species

Target PTMs	CW type	Plants used	References
Se	NA	*Typha latifolia*	Etteieb et al. (2021)
Fe, Al, Zn, Co, Ni, Cr	NA	*Typha latifolia*	Singh and Chakraborty (2021)
Zn, Cr, Ni, Pb	SSF (hybrid, VFCW followed by a HFCW)	*Phragmites australis*, *Chrysopogon zizanioides*	Saeed et al. (2021)
As, Fe, Pb	HFCW	*Phragmites australis*	Lizama-Allende et al. (2021)
Cs, Pb	VFCW	*Chenopodium album*, *Amaranthus cruentus*, *Phragmites australis*, *Bambusa vulgaris*	Moogouei and Chen (2020)
Cu, Pd, Zn, Cd	FWSCW	*Phragmites australis*, *Typha latifolia*	Gill et al. (2017)
Pb, Cu, Zn, Co, Cr, As, Ni	HFCW	*Typha latifolia*	Rai et al. (2015)
Cu, Pd, Ni, Zn	HFCW	*Phragmites australis*	Pedescoll et al. (2015)
Cr, Ni	VFCW	*Canna indica*	Yadav et al. (2010)
Zn, Hg, Cr, As, Se	FWSCW	*Typha angustifolia* L., *Schoenoplectus californicus*	Dorman et al. (2009)
Cd, Cr, Fe, Pb, Cu, Ni	FWSCW	*Typha latifolia*, *Phragmites australis*, *Ceratophyllum demersum*, *Alisma plantago-aquatica*	Khan et al. (2009)
Cu, Pd, Ni, Zn, Hg	HFCW	*Phragmites australis, Phalaris arundinacea*	Kröpfelová et al. (2009)
Cu, Pd, Ni, Zn	HFCW	*Phragmites australis*	Lesage et al. (2007b)
Mn, Ni, Zn, Cd, Cu, Pb, Sr, V	HFCW	*Phragmites communis*, *Salix viminalis*	Samecka-Cymerman et al. (2004)
U	NA	*Eleocharis dulcis*	Overall and Parry (2004)

NA not available

including metallothioneins and phytochelatins which help in forming metal-chelate complexes (Palmer and Guerinot 2009; Verbruggen et al. 2009; Pal and Rai 2010).

Rhizosphere in the CWs also provides suitable environment to various soil microbes for their proliferation. The most commonly found rhizobacteria include *Azotobacter*, *Pseudomonas*, and *Rhizobium*. Microbes can also directly or indirectly affect the metal removal process in CWs via biosorption and microbial oxidation-reduction of metals (Kosolapov et al. 2004). As mentioned above, microorganisms can promote Fe or Mn oxidation or sulfate reduction which consequently leads to the co-precipitation of metals with Fe or Mn (oxy)hydroxides or sulfide as insoluble metal sulfide (e.g., FeS, CuS, ZnS) (Fortin et al. 2000; Marchand et al. 2010; Sochacki et al. 2018). Anaerobic metal-reducing bacteria can also govern the reduction of toxic metals to insoluble and less toxic form, for example, microbial reduction of Se oxyanion to Se(0) or Cr(VI) to Cr(III) (Kosolapov et al. 2004; Zhao et al. 2020).

Mustapha et al. (2018) compared the removal performance of three plant species (*Cyperus alternifolius*, *Cynodon dactylon*, and *Typha latifolia*) in a pilot-scale VFCW for the removal of PTMs from the wastewater. The VFCW with *T. latifolia* showed the best PTM removal performance, followed by *C. alternifolius* and *C. dactylon* (Mustapha et al. 2018). The metal uptake rate per unit area of the wetland is generally higher for perennial plants or macrophytes such as cattails (Sochacki et al. 2018). *Phragmites australis* and *T. latifolia* are among the mostly used hyperaccumulator plant species for the removal of various PTMs from the wastewater in CWs (Sochacki et al. 2018; Batool and Saleh 2020). Both *P. australis* and *T. latifolia* also show strong metal tolerance which is vital for their application in CWs. Various other plant species such as *Canna indica*, *Iris pseudacorus*, *Scirpus americanus*, and *Stenotaphrum secundatum* have also been employed successfully in CWs for the better metal removal performance (Mal and Rangabhashiyam 2021). *Myriophyllum spicatum* was employed in CWs for the removal of Co, Cu, Ni, and Zn from industrial wastewater, where it involves a combination of biosorption, accumulation, and translocation of metals in the plant biomass (Lesage et al. 2007a, b). Aslam et al. (2007) reported a gradual increase in metal (Cu, Zn, and Fe) removal with the growth of plants and biofilm from a wastewater of an oil refinery, and 35–56% of the metals was taken up by *Phragmites* plant biomass. Hadad et al. (2006) demonstrated the removal of Cr, Fe, Ni, and Zn from an industrial wastewater in CWs, where *Typha domingensis* dominated among other species. In contrast, Mantovi et al. (2003) reported that *P. australis* played a non-significant part during the treatment of dairy effluent by HFCW as only 1–2% of metal (Cu and Zn) was accumulated in the plant biomass. However, organic matter will be limited over time in unplanted CW, as the microbes will keep utilizing substrate and substrate capacity to metal immobilization will decrease over time due to the saturation of binding sites.

Seasonal effect on the metal removal efficiency of planted CWs cannot be ignored as well (Rai et al. 2015; Mulkeen et al. 2017; Rahman et al. 2020). Active plant metabolism along with faster biochemical processes due to higher temperatures in summer compared to winter results in better metal removal. For example, in the presence of *P. australis* and *P. canadensis*, Cu removal was 30% and 22% higher in summer than in winter, respectively. Similarly, Zn removal was 18% and 92%, Pb removal was 26% and 33%, and Cd removal was 229% and 17% higher in summer (Samecka-Cymerman et al. 2004). Recently, Moogouei and Chen (2020) demonstrated removal of Pb and Cs from the wastewater in a hydroponic CW where aquatic and terrestrial plants including *Amaranthus cruentus*, *Bambusa vulgaris*, *Chenopodium album*, and *P. australis* were used for phytoremediation. *Callitriche stagnalis* Scop., *Potamogeton natans* L., and *Potamogeton pectinatus* L. also showed promising U accumulation and removal from the wastewater in a prototype hydroponic CW.

4.5.5 Effect of Artificial Aeration (AA) on the Performance of CWs

If sufficient oxygen within the system is available, it gives microorganisms the conditions to complete biodegradation, reduces the clogging, and also enhances the removal efficiency of the system for organic matter and nutrients (nitrogen and phosphorus) (Ilyas and Masih 2017a, 2018) and consequently reduces the land area required by CWs (Ilyas and Masih 2017b). Several studies examined the effect of AA on the performance of CWs for the removal of nutrients (nitrogen and phosphorus) and organic matter (e.g., Ilyas and Masih 2017a, b, 2018), PhCs (Ilyas and van Hullebusch 2020c), PCPs (Ilyas and van Hullebusch 2020a), SHs (Chen et al. 2021), petroleum hydrocarbons (Wallace et al. 2011; Al-Baldawi et al. 2013), azo dyes (Ong et al. 2011), and metals (Mozaffari et al. 2021).

Li et al. (2017c) investigated the effect of AA on a laboratory-scale FWSCW for the removal of organic contaminants (PhCs and PCPs) from the wastewater. Few studies investigated the effect of AA on VFCW and HFCW for the removal of PhCs and PCPs (Ávila et al. 2014b; Kahl et al. 2017; Nivala et al. 2019). Ávila et al. (2014b) concluded that the saturated CW with AA performed similar to the typical unsaturated CW. Similarly, Auvinen et al. (2017a, b) studied the effect of AA on a pilot-scale HFCW and a laboratory-scale HCW, respectively, for the removal of PhCs. The removal efficiency of a few of the targeted PhCs was found to be dependent on the applied AA. This is explicit by the enhanced removal efficiency of the studied PhCs and PCPs in the case of AA-FWSCW (caffeine and triclosan), AA-HFCW (diclofenac, ibuprofen, naproxen, caffeine, sotalol, and acesulfame), AA-VFCW (diclofenac, naproxen, carbamazepine, triclosan, tonalide, oxybenzone, and acesulfame), and AA-HCW (diclofenac, carbamazepine, and sotalol) compared with their removal efficiency in the corresponding NA-CWs. For instance, the removal efficiency of diclofenac in NA-HFCW, NA-VFCW, and NA-HCW was 21 ± 12%, 56 ± 7%, and 56 ± 32%, respectively, which was enhanced in their corresponding AA-CWs (48 ± 22%, 68 ± 9%, and 99%, respectively) (Ilyas and van Hullebusch 2020c). Similarly, the removal efficiency of triclosan was enhanced in AA-FWSCW compared with NA-FWSCW (99% and 94%, respectively) (Li et al. 2017b) and in AA-VFCW compared with NA-VFCW (86% and 73%, respectively) (Ávila et al. 2014b). The available evidence on the effect of AA to enhance the performance of CWs for the removal of PhCs and PCPs is comprehensively synthesized in Ilyas and van Hullebusch (2020a, c). Chen et al. (2021) investigated the performance of a laboratory-scale AA-VFCW, NA-VFCW, AA-HCW, and NA-HCW (combination of VFCW and HFCW) for the removal of SHs from the wastewater. Among the detected SHs were 4-hydroxy-androst-4-ene-17-dione, 17β-boldenone, androsta-1,4-diene-3,17-dione, 4-androstene-3,17-dione, chlormadinone, epiandrosterone, testosterone, progesterone, and stanozolol. The concentration of the detected SHs ranged from 0.007 to 3.04 μg/L, and the removal efficiency ranged from 15% to 100% in the studied types of CWs. The authors reported the high total removal efficiency of the detected SHs by AA-VFCW (98%) compared with NA-VFCW (37%) and by AA-HCW (~99.8%) compared with NA-HCW (ranged from 42% to 65%). Although in NA-HCW the NA-HFCW was a good supplement (ranged from 10% to 33%) to improve the total removal efficiency, in the case of AA-HCW, the high removal efficiency was achieved in AA-VFCW indicating that AA-HFCW was not needed. Therefore, the authors suggested that for the field application of CWs, the AA-VFCW may be better for urban areas with limited space considering the high removal efficiency of a single system.

Wallace et al. (2011) studied the performance of two full-scale AA-VFCWs for the removal of organic compounds from oil refinery wastewater in cold climates. The AA was applied to prevent the freezing of water in VFCWs. The authors demonstrated the high potential of AA-VFCWs for the removal of BTEX, which is evident by its complete removal (100%) at temperatures below −20 °C. This indicates that the performance of a single CW system can be significantly enhanced by the application of AA for the removal of BTEX. Al-Baldawi et al. (2013) examined the performance of a laboratory-scale AA-HFCW and NA-HFCW for the removal of petroleum hydrocarbons. The results showed the significantly higher removal efficiency of total petroleum hydrocarbons with diesel concentrations of 0.175% and 0.25% in AA-HFCW (85% and 91%, respectively) compared with NA-HFCW (71% and 67%, respectively). Ong et al. (2011) examined the performance of a laboratory-scale AA-VFCW and NA-VFCW for the removal of azo dyes such as acid orange 7 from the wastewater. The results showed the high removal efficiency of acid orange 7 (above 94%) in AA- and NA-VFCWs; however, the AA-VFCW performed better than the NA-VFCW for the removal of COD (95% and 62%, respectively) and aromatic amines generated from the reduction of azo dye. Mozaffari et al. (2021) demonstrated the metal removal in an AA-HFCW. The results showed that the maximum removal efficiency of Fe, Mn, aluminum, Zn, Cu, Ni, Pb, and Cr was 98%, 81%, 73%, 100%, 80%, 85%, 99%, and 92%, respectively, which was attributed to oxyhydroxide precipitation or co-precipitation under aerobic condition.

4.6 Conclusions

This chapter synthesizes the available knowledge on the sources of selected categories of organic contaminants (priority substances: PAHs, petroleum hydrocarbons, azo dyes, and chlorinated solvents; and EOCs: PhCs, PCPs, SHs, and pesticides) and inorganic contaminants (nutrients, metal(loid)s, and radioactive compounds) in water resources and the environment as well as the societal challenges related to their discharge. The available bioremediation techniques (microbial remediation (microbes (e.g., bacteria)), mycoremediation (fungi), phycoremediation (algae), and phytoremediation (plants)) for the treatment of wastewater containing these types of contaminants are described, and the concept of CWs (phytoremediation technique) is discussed in detail. The following specific conclusions can be inferred from this research:

1. Both the natural processes (e.g., chemical weathering, volcanic fallout, plant decay, atmospheric inputs, aeolian erosion, recycled oceanic aerosols, leaching of organic soils, and primary production and respiration) and anthropogenic activities (e.g., mining, extraction or refining ores, agricultural drainage due to use of pesticides and chemical fertilizers, various industries including petrochemicals, dyes and paints, PhCs, PCPs, tanning, paper and pulp, alloys or metal plating, batteries, and automobiles) contribute to the discharge of selected categories of organic and inorganic contaminants to water resources and the environment.
2. Although these organic contaminants are found to be in relatively small concentrations (e.g., ng/L to μg/L) in water resources, their presence (e.g., as individual compounds, TPs, and multitude of compounds) poses risk to aquatic and terrestrial life. Furthermore, the higher concentration of these organic compounds compared with their potential no-effect concentration poses severe risk to human health, since many of these compounds are considered as prospective EDCs, cytotoxic, mutagenic, and carcinogenic.
3. The inorganic contaminants also pose a serious threat due to their toxic effect on the environment and human health. For instance, although some PTMs (e.g., Zn, Cu, Fe, Ni) are essential micronutrients, these are harmful after certain level (e.g., beyond permissible limit) because these are nonbiodegradable and have a tendency to bioaccumulate via food chain and biomagnify along the trophic levels, which makes it a serious concern for living organisms even at small concentration.
4. The bioremediation techniques such as microbial remediation (microbes (e.g., bacteria)), mycoremediation (fungi), phycoremediation (algae), and phytoremediation (plants) are environmentally friendly, cost-effective, and sustainable techniques, which show a certain potential to remove selected categories of organic and inorganic contaminants from the wastewater. For instance, in the complex CW system, the occurrence of several elimination pathways such as physical processes (e.g., volatilization, sedimentation, adsorption/sorption), chemical processes (e.g., oxidation, reduction, and photolysis (FWSCW)), and biological processes (e.g., microbial degradation, rhizofiltration, and phytoremediation) contribute to remove pollutants (organic and inorganic) from the wastewater.

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Biological Treatment of Volatile Organic Compounds (VOCs) and Odorous Compounds

5

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Abstract

The increasing human population necessitates the creation of high-quality habitats and pure natural resources. Due to the growth of industries and other anthropogenic activities, the amounts of volatile organic compounds (VOCs) and odorants increase in the environment. Thus, the generation of high-quality effluent using appropriate treatment technology has become an essential requirement. These critical needs can be achieved with the aid of physical, chemical, and biological treatment technologies. The biological treatment techniques are considered to be the most advantageous technology for the treatment of volatile organic compounds (VOCs) and odorants because biological treatment technologies offer a cost-effective and environmentally friendly alternative to other pollution control technologies. The diverse biological treatment approaches for volatile organic compounds (VOCs) and odorants in bulk size and lab-scale research are discussed in this chapter.

Keywords

VOC · Biofilters · Bioscrubbers · Biotrickling · Odorants

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5.1 Introduction

Natural and man-made activities are the major sources of volatile organic compounds (VOCs) and odorous compounds. However, man-made necessities such as industrialization and improper industrial waste treatment are considered the main source of VOCs and odorous compounds. These emitted VOCs and odorous compounds cause adverse effects on environmental health. Thus, it is necessary to provide nuisance-free breathable air for a sustainable environment. The only approach to control VOC emissions from industries is to enact laws by the government bodies. Similarly, residents can help to decrease VOCs and odorous compounds in urban areas by receiving sufficient training from government agencies. Finally, the emitted VOCs from industries, bio-waste, etc. can be controlled through their proper treatment. Several treatment methods are successfully introduced in lab-scale and bulk-scale operations. Based on the results, the treatment methods are classified into chemical (thermal oxidation, catalytic oxidation, ozonation), physical (condensation, adsorption, absorption), and biological (using biofilters, biotrickling filters, bioscrubbers, and other bioreactor types) methods based on their mode of action. Biological methods are the most promising among these techniques as they are more environmentally friendly than physical and chemical methods. Moreover, they do not require the use of chemicals, can be conducted at normal temperatures (10–40 °C) and atmospheric pressure, and are less costly, simple to operate, and ecologically clean because the processes of microbial degradation are generally oxidative in nature and produce ecologically safe end products such as carbon dioxide, water, sulfate, and nitrates.

The following section will describe the different sources and adverse effects of VOCs, followed by explaining the different methods of biological treatment of VOCs.

5.1.1 Volatile Organic Compounds (VOCs)

The ability of a substance to vaporize quickly is stated as its volatility. Organic compounds having high vapor pressure, low boiling point, and low water solubility at room temperature are collectively known as volatile organic compounds (VOCs). The European Union defines a VOC as “any organic compound having an initial boiling point less than or equal to 250 °C (482 °F) measured at a standard atmospheric pressure of 101.3 kPa.” A volatile organic compound (VOC) is defined by the US Environmental Protection Agency (EPA) as “any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.”

Volatile organic compounds (VOCs) are a class of small (molecular weight 50–200 Da) stable molecules that are volatile at room temperature and exhibit lipophilic characteristic. VOCs are responsible for the odor of perfumes and scents, as well as pollution. They play an important role in animal-plant communication, such as pollinator attractants and predation protection, and even in inter-plant interactions. VOCs are emitted to the atmosphere mainly through biological matrices and anthropogenic sources. Most of the VOCs found in the earth’s atmosphere are biogenic. Biogenic volatile organic compounds (BVOCs) are VOCs emitted by plants, animals, or microorganisms, and most commonly, they are terpenoids, alcohols, and carbonyls. Plants are the primary source for VOC emission from biological matrices. It is estimated that biological sources emit 760 Tg of carbon per year in the form of VOCs (Sindelarova et al. 2014). Anthropogenic sources emit about 142 Tg (1.42 × 1011 kg) of carbon per year in the form of VOCs (Goldstein and Ian 2007). The primary sources of man-made VOCs are combustion of fossil fuel; manufacturing industries; solvents used in coatings, indoor paints, and inks; use of biofuel; and combustion of biomass.

5.1.2 Classification of VOCs

5.1.2.1 On the Basis of Boiling Points

The VOCs are classified into three categories on the basis of boiling points—very volatile organic compounds, normal VOC, and semi-volatile organic compounds.

- **Very volatile organic compounds (VVOCs):** VVOCs are extremely volatile, making their measurement challenging. They are primarily found in the atmosphere rather than on surfaces or in materials. These have a boiling point from 0 to 50–100 °C. Examples are methyl chloride, propane, etc.
- **Volatile organic compounds (VOCs):** Compounds containing carbon with a boiling point less than 250 °C at 101.3 kPa pressure. Examples are acetone, ethanol, toluene, etc.
- **Semi-volatile organic compounds (SVOC):** Organic compounds have a boiling point higher than water (240–400 °C) and are vaporized at room temperature. Examples are polynuclear aromatic hydrides, phenol, etc.

5.1.2.2 On the Basis of Sources

On the basis of sources, in which VOCs are forming, the compounds are classified into two categories such as natural VOCs and human-made VOCs.

- **Natural VOCs:** They are released into the environment as a result of bacterial oxidation of organic matter or the biodegradation process. These are also obtained through gaseous emission by conifers and deciduous trees, flower perfume, and respiration. Terpenoids and fatty acid derivatives are the major classes of VOCs produced by plants.
- **Human-made or anthropogenic VOCs:** Human activities also produce a wide variety of volatile organic compounds. VOCs are produced by incomplete combustion of fossil fuels or unintended evaporation of fuels, the most common of which is ethane, a relatively inert compound. Compressed aerosol products, primarily butane and propane, are estimated to emit around 1.3 billion tonnes

of VOCs globally each year (Yeoman and Lewis 2021). Paint is one of the most well-known VOC-containing materials. VOCs are used in paints to improve their overall look and quality. Aliphatic hydrocarbons, ethyl acetate, glycol ethers, and acetone are the typical solvents used in paints. Wood-based building materials have been identified as significant indoor sources of volatile organic compounds (VOCs), accounting for 60% of total VOC emissions (Loftness et al. 2007). Anthropogenic VOCs are legally restricted, particularly indoors, where concentrations are highest.

5.1.3 Effects of VOCs on Humans

The toxic effect of organic chemicals is mainly due to the level of exposure and the length of time exposed. The majority of VOCs are not acutely toxic, but they may have long-term chronic health consequences. The release of volatile chemicals is called off-gassing, and it continues over the years. Respiratory, allergic, or immune effects in infants or children are associated with anthropogenic VOCs. Formaldehyde, a commonly used VOC in regular paints, is a carcinogen (Agency for Toxic Substances and Disease Registry 2016). Polyurethanes found in modern paints are harmful to the respiratory system. Paints containing lead- and mercury-based substances are hazardous to our health. The aromatic fumes evolving from organic solvent-based paints contain epoxy resins. The inhalation of the smoke over a long period causes headaches, convulsions, central nervous system damage, nausea, dizziness, kidney and liver damage, fatigue, and sick building syndrome (Prien and Traber 1988). People with weakened immune systems may experience eye irritation, nose and throat discomfort, and allergic skin reactions as a result of their exposure to VOCs. Furthermore, VOCs have been linked to lung, stomach, and kidney cancer. Moreover, VOC exposure can disrupt infant growth in pregnant women, and ethyl glycol in paints causes birth defects in newborn children (Woolf et al. 1992). Some VOCs, such as styrene and limonene, can react with nitrogen oxides or ozone to form new oxidation products and secondary aerosols that can cause sensory irritation.

5.1.4 Effects of VOCs on Environment

VOCs are also known to harm our mother nature. When VOCs are exposed to sunlight, they emit greenhouse gases that eventually form a ground-level smog layer in the atmosphere (Association for Energy Affordability Energy and Environment 2007). This smog is harmful to our planet's protective ozone layer. These greenhouse gases react with rain and make it acidic; acid rain has an impact on the soil roof, water bodies, plants, and animals that live within them. Furthermore, the harmful emissions from VOCs affect the overall climate and contribute to global warming (Ghirardo et al. 2020). The entire food cycle is impacted indirectly, and it eventually reaches us. When the effects of VOCs are combined, the dangers are limitless. By giving proper awareness and implementing strict environmental protection policies, such risks can be eliminated. Low VOC paints are becoming increasingly popular in the paint industry. According to a recent market report, the low VOC paint market is expected to grow at a compound annual growth rate (CAGR) of 6.5% over the next 5 years. Today, 83% of people are opting for water-based paints than latex paints. This is happening as people become more aware of the harmful effects of VOCs and due to the strict federal limits imposed.

5.1.5 Odor Compounds

An odor is a volatile chemical compound that humans and other animals perceive through their sense of smell, also known as olfaction. They are also known as aromas or fragrances, and the unpleasantness is called by the words reeks, stenches, and stinks. An aroma compound or an odorant is a type of molecule that produces an odor. These compounds have small molecular weights (less than 300 Da) and are easily dispersed in air, because of their high vapor pressure. Odors can be detected even in extremely low concentrations. Nitrogen compounds such as ammonia (NH_3), sulfur compounds such as hydrogen sulfide (H_2S) and mercaptans, organic acids, aldehydes, and hydrocarbons are the most significant odorous gases (Brinkmann et al. 2016).

5.1.6 Sources of Odor Compounds

On focusing on human welfare, the sources are concentrated mainly on anthropogenic activities. Agricultural waste, food processing industries, municipal solid waste composting, livestock production industries, semiconductor industries, paint shops, oil refineries, pulp and paper mills, plastics and resin manufacturing, various chemical industries, and the incomplete combustion of hydrocarbon fuels in a variety of industries are the major sources of odorous compounds (Bordado and Gomes 2003; Chen et al. 2016). Odorous carbonyl compounds are released into the atmosphere due to the use of ethanol in industries. The odor activity value (OAV), which is the ratio of concentration to the odor threshold value, can be used to assess the activity of odorous VOCs (Wu et al. 2015). The compound with the highest OAV is thought to be the primary source of odor.

The bio-solids formed due to the biological and anthropogenic activities are significant sources of nuisance emission. The volatile sulfur compounds (VSCs) are widely attributed as the dominant odorants emitted from anaerobically stabilized bio-solids. Biotic or abiotic degradation of organic material is another source of odorous VOCs and VSCs. The degradation of proteins produces volatile nitrogenous compounds such as ammonia and trimethylamine (TMA), which have been reported to be emitted from land-applied dewatered sludge (Rosenfeld et al. 2001). The wood-based material plays an important role in the emission of odorous compounds because wood is mostly made up of biopolymers, cellulose, hemicellulose, and lignin, with trace amounts of inorganic compounds and extractives. The extractives, which are found in the resin duct, gum duct, and parenchyma cells, are responsible for the majority of odorants and also contain aliphatic compounds, terpenes, terpenoids, and phenols. Commercial animal husbandry has an important role in the emission of nuisance odors. Indoles and skatole emitted by animal facilities have also been demonstrated to have distinct toxicological effects (Spoelstra 1977).

5.1.7 Effect of Odorous Compounds

The VOC and carbonyl compounds found in malodors have a negative impact on the air quality in the areas surrounding the sources and the health of those who live nearby. This type of air pollution can cause the following effects: deterioration of environmental quality; interference with business activities; discomfort, harm, or safety risks to any person; and disruption in the use of any property, plant, or animal. As a result, many countries are attempting to develop effective odor regulations or guidelines to reduce their concentrations in ambient air. The presence of some toxic volatile organic compounds (VOCs) and carbonyl compounds in odorous compounds makes monitoring of odorous compounds in ambient air an essential task for environmental researchers. Many researchers have reported the concentrations of odorous compounds in the atmosphere around the world in recent years, about their hazardous and/or toxic nature to humans (Korpi et al. 2009; Kotowska et al. 2012; Lee et al. 2013; Lehtinen and Veijanen 2011; Loftness et al. 2007). In many countries, odors are now subjected to control and regulations, and specific methods for odor measurement have been developed. These methods include both sensory and instrumental techniques. The following are the most crucial odor measurement methods: dynamic olfactometry, chemical analysis (with speciation or non-specific), gas chromatography-olfactometry (GC-O), tracer analysis, instrumental odor monitoring by e-noses, field inspection, field olfactometry, and citizen science. The only odor measurement methods that have been standardized at the European level are dynamic olfactometry and field inspection (Loftness et al. 2007; Yokoyama and Carlson 1981; Pal et al. 2008). Other techniques, such as chemical characterization, are consolidated analytical techniques that are commonly used to provide information about the odor properties of gaseous mixtures. Methods based on citizen science, on the other hand, are relatively new. These techniques, which rely on citizens' active participation, have been proposed in recent years to address socio-environmental conflicts within impacted communities (Rabaud et al. 2003; Rao 2007).

5.1.8 Common Removal Methods

In recent years, various technologies have been developed to improve air quality and reduce or eliminate air pollution caused by VOCs and odorous gases (Capelli et al. 2019). The most common methods used can be divided into three categories:

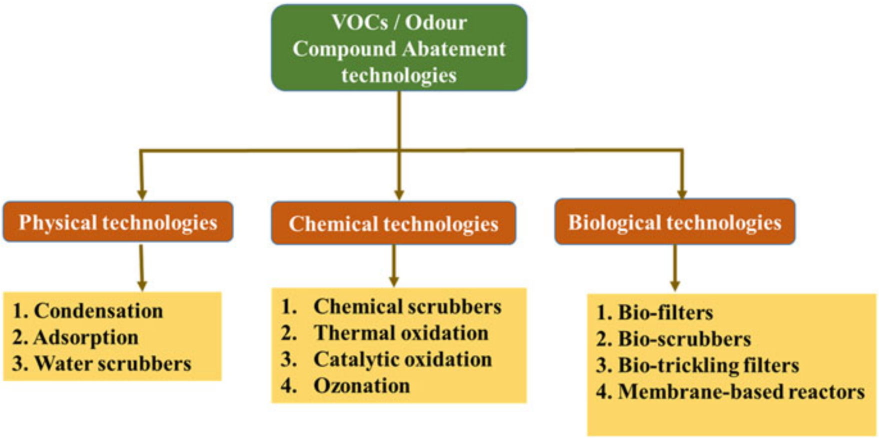

Fig. 5.1 Different methods for VOCs and odorous gas abatements

physical technologies (condensation, adsorption, and water scrubbers), chemical technologies (chemical scrubbers, thermal oxidation, catalytic oxidation, and ozonation), and biological technologies (biofilters (BF), bioscrubbers, and biotrickling filters (BTFs)) (Mudliar et al. 2010). Physical and chemical technologies have been widely used because of their low empty bed residence time (EBRT) leading to compact equipment and rapid startup, extensive experience in design and operation that has been accumulated over several decades, and suitability for large-flow waste gas streams and high pollutant concentration. Despite providing acceptable VOC removal rates, physicochemical treatments are more expensive than biological treatments (Fig. 5.1).

5.1.9 Why Biological Methods?

The physical and chemical treatment methods have some drawbacks, such as incomplete removal; the need for expensive equipment, monitoring systems, and reagents; high energy requirements; and the generation of undesirable by-products that must be disposed of. Furthermore, these methods may be ineffective and inefficient. Biological odor abatement methods are more environmentally friendly than physical and chemical technologies because they do not use chemicals and can be carried out at normal temperatures (10–40 °C) and atmospheric pressure. Biological methods such as bioscrubbing and biofiltration are less expensive, easier to operate, and more environmentally friendly than physicochemical treatments because microbial degradation processes are generally oxidative in nature and produce ecologically safe end products such as carbon dioxide, water, sulfate, and nitrate (Revah and Morgan-Sagastume 2005; Estrada et al. 2011; Bindra et al. 2015). Because wide ranges of VOCs are biodegradable, they can be biologically treated with organisms that are specific to the type of VOC to be destroyed. Esters, benzene, toluene, and phenols are examples of easily biodegradable VOCs. Bio-treatment of VOCs may offer advantages over more traditional processes, such as lower operating and capital costs and a lower carbon footprint. This is due to lower energy requirements because microorganisms metabolize organic compounds at room temperature rather than relying on heat or radiation.

5.2 Biological Methods

Nowadays, biological waste treatment process using bioreactors for both the VOCs and odor compounds attracts more importance over conventional technologies because bioreactors offer a cost-effective and environment-friendly methodology for treating VOCs and odor compounds. The major popularity of biological treatment over physical and chemical methods is its environment-friendly approach (Devinny et al. 1999; Delhomenie and Heitz 2005). The abatement technologies are designed based on the nature and property of the pollutant and the technology adopted for the treatment. The main parameters considered for the pollutants are the flow rate of pollutant, the concentration of emissive pollutant, and the property of the pollutant molecule emitted (such as solubility, acidity, basicity, adsorbability, and biodegradability). Furthermore, considering the techniques such as the efficiency of the technique adopted for the particular at various time intervals pollutant and generation of secondary pollutants, the energy consumption of the methods, space required for the techniques, and the operation and maintenance requirements of the techniques, the technologies.

The widely used bioreactors for the treatment of VOCs and odorous compounds are (1) biofiltration (BF) reactors, (2) biotrickling filtration (BTF) reactors, (3) bioscrubber reactors, and (4) membrane-based reactors (MBRs). These systems have differences in their complexity, process design, equipment dimensions, and working parameters. However, they act as a good solution for the removal of both VOCs and odorous compounds. Each reactor differs from the environment of the microorganisms (suspended or fixed) and the state of the liquid (flow or stationary). Biological waste air treatment technology makes use of several types of bioreactors depending on the load and kind of pollutant to be treated. The type of bioreactor used for abatement has a direct consequence on the efficiency of the treatment process. For sewer gas treatment technologies, activated carbon column, biofilter (BF), and biotrickling filtration (BTF) reactors are commonly used. According to Estrada et al. the operating cost of a conventional activated carbon system is 6 times and 3.6 times higher than the costs of BTF and BF, respectively (Estrada et al. 2012). Both BF and BTF are fixed-bed bioreactors in which active microorganisms are immobilized in the reactor.

5.2.1 Biofilters

A biofilter is the mainstream deodorization technology used in biological methods. The biofilters are air-phase biological reactors used for treatment of industrial air pollutants, which include odorous compounds such as hydrogen sulfide and ammonia or volatile organic compounds (VOCs) such as benzene and toluene. Biofilters (BFs) are reactors in which a humid polluted air stream is passed through a porous packed bed on which a mixed culture of pollutant-degrading organisms is immobilized (Mudliar et al. 2010). The US Environmental Protection Agency classified more than 180 compounds as hazardous air pollutants (HAPs), which can cause serious health and environmental problems. Many of the listed HAPs are VOCs that can be treated by biofiltration. In the last two decades, biofilter technology is based on bio-oxidation process that has gained importance for industrial air treatment over conventional technologies due to many advantages. The VOCs and odorous gases flow through the porous packing media, where the immobilized microbial film oxidizes the polluted gases through biological oxidation process. BFs are used to treat a wide variety of organic and inorganic pollutants in industrial and municipal exhaust streams. Although traditionally used for the treatment of odorous gases from sewage treatment plants and composting facilities, BFs now find wide application in the treatment of several VOCs and odorous compounds (Devinny et al. 1999). Interactions between bio-oxidation process and mass transfer effects of pollutants in the gas as well as biofilm phases make this process complex. The waste gases, after entering the biofilter, encounter microorganisms attached to the surface of the filter and are captured and degraded by the microorganisms to achieve deodorization. In Europe, more than 600 chemical processing industries use BFs to deodorize and treat VOCs. BFs are typically used for the treatment of large volumes of air streams containing a low concentration of VOCs or odorants.

VOCs and odors are two important gaseous pollutants escaped from landfills, which are harmful to human health and the surrounding environment. Biofilter was used to control VOCs and odors from an actual landfill. The VOC and odor gas treatment mechanisms by the biofilters in various zones include identifying gaseous pollutant components, monitoring the removal efficiency of the biofilters, and studying the evolutionary changes of the bacterial population during operations. The studies carried out by Lin et al. revealed that the gaseous VOCs and odor compounds produced in the sealing and leachate treatment zone are appreciably different (Lin et al. 2012). Biofilters in both zones have good removal efficiency for TVOCs, sulfide and amine. This is because the bacterial population of biofilters in different zones have been completely different after a long period of operation. The analysis of gaseous pollutants and bacterial population distribution in the different layers of biofilter showed that the concentration of gaseous pollutants and bacterial diversity in the two biofilters decreased from the lower layer to the upper layer. The average removal rate of the total VOC (TVOC), sulfides and amines, in both biofilters exceeded 80%. The outlet concentrations meet the level 3 standard of the emission standards for odor pollutants (GB 14544–93). This is mainly related to the evolution of bacterial population during the operation of biofilters. In the inoculums,

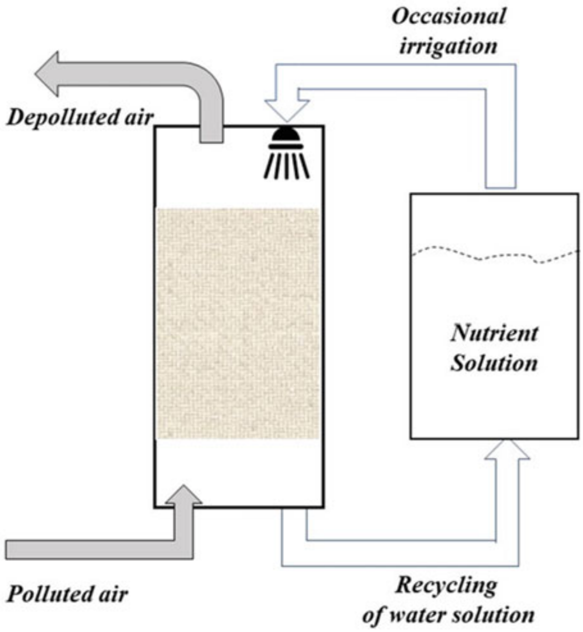

Fig. 5.2 Schematic representation of a biofilter unit

the dominant bacterial genus is *Brevibacillus* (58.84%), and bacteria with *Bacillus* and *Pseudomonas* only occupied 2.67% and 1.77%. With the extension of operation time, the dominant bacteria of biofilter in the sealing zone gradually evolved into *Mycobacterium* (67.82%) and *Bacillus* (27.90%), while the dominant bacteria of biofilter in the leachate treatment zone evolved into *Bacillus* (72.69%) and *Pseudomonas* (21.59%). These results indicated that identifying gaseous pollutant components and designing appropriate treatment systems based on their components will further improve the operating efficiency of biofilters in the actual landfill (Yunping et al. 2020; Tianlong et al. 2021; Cheng et al. 2010; Paula et al. 2021; Li et al. 2016) (Fig. 5.2).

In North China (30,000 m^2 area landfill site), three biofilters were deployed to remove excess H_2S and NH_3. Results showed that the inlet concentrations of H_2S and NH_3 were 16.4–220.3 mg/m^3 and 2.0–56.4 mg/m^3, respectively (Mee 2018). Outlet concentrations were reduced to 1.0–33.1 mg/m^3 for H_2S and 0–9.2 mg/m^3 for NH_3. H_2S and NH_3 were both treated effectively by the biofilters in an average of 81% each. A high elimination capacity was obtained in the biofilter harvesting high inlet load. High-throughput sequencing technology was utilized to assay the microbial populations in the biofilters. Their characteristics and distributions in the biofilters depended on the inlet concentration of substrates and the microenvironment within the packing materials (Jiaqi et al. 2016). The results from this bio-product analysis indicated that most of H_2S were bio-oxidized into sulfur and sulfate, while NH_3 was converted into nitrate or dissolved into the liquid phase mainly by absorption or chemical neutralization in the biofilters (Lee et al. 2018).

5.2.1.1 Biofilm Formation in Biofilters

Polyurethane (PU) sponges are popular packing material in biofilters, and their smooth and hydrophobic surface often leads to an uneven distribution and detachment of biofilms. An investigation carried out on benzene, toluene, ethylbenzene, and xylene (BTEX) removal by Mathur et al. (2012) showed that the biofilters had a highly efficient BTEX degradation ability (Loftness et al. 2007). *o*-Xylene is one of the major toxic pollutants cited by the US Environmental Protection Agency (EPA), applied widely as diluents and solvents in the printing, rubber, and leather industries. The wastewater and waste gas generated in the above production process are the main sources of *o*-xylene in the environment. A 62% of removal efficiency with a maximum elimination capacity (188 g/m^3 h) for BTEX in biofilters over 212 days of continuous operation was also reported (Bordado and Gomes 2003; Brinkmann et al. 2016). The packing material is significant for the formation of biofilms since it provides a side on which microorganisms may grow, and its sorption effects also ensure contact between gaseous pollutants and microorganisms. The packing material directly affects the removal efficiency and the operational stability of a reactor. Therefore, the packing material is always considered to be the core component of a biofilter. Polyurethane (PU) sponges were commonly used because of their advantages of easy access, low cost, and high resilience compared with other packing materials. However, the surface of a PU sponge is usually not conducive to biofilm formation due to its oxidation film and smoothness, which limits the application and performance of biofilter (Chen and Hoff 2009). Z. sun et al. (2020) developed and modifed polyurethane sponge as biofilter's packing materials to attain a high surface roughness and positive charge. This modified biofilter had superior and more action in the microbial growth and viability, structure, and microbial adhesive strength than normal biofilter. In addition, the performance in biofilters for BTEX removal also showed the application potential of the modified PU sponge (Goldstein and Ian 2007). As the polluted gas stream passes through the filter media, VOCs or odorous compounds in the gas are partitioned into the biofilm where biological oxidation occurs under aerobic conditions. The main advantage of biofiltration is that the pollutants are converted into harmless end products. Relatively low costs and excellent operational stability are also recognized as the advantages of biofiltration approaches (Rosenfeld et al. 2001).

The empty bed retention time (EBRT) is another important factor in assessing biofilter performance. It involves microorganism absorption and conversion process. Li et al. reported that the average removal efficiency of *o*-xylene with biofilter is 93.5% under a stable operation with bacteria *Pseudomonas* sp., *Sphingomonas* sp., and *Defluviicoccus* sp. and the fungi *Aspergillus* sp. and *Scedosporium* sp. Good biodegradation efficiencies could be achieved in the treatment of waste gases containing *o*-xylene using the integrated bioreactor (Mudliar et al. 2010). Some of the odorous and VOCs and their respective microbial species are listed in Table 5.1 (Takeuchi et al. 2001; Prakash et al. 2012; Cho et al. 2017; Chune et al. 2015). Odor emission is one of the most common problems associated with dead animal composting. The biofiltration treatment for eliminating exhaust odors formed during dead pig and manure composting has been studied by (Shang et al. 2021). They

Table 5.1 Biofiltration systems to decompose different VOCs/odorous compounds

Compound	Taxonomy	Microbial species
NH_3	*β-Proteobacteria*	*Nitrosomonas europaea*
		Nitrosospira sp.
		Stenotrophomonas nitritireducens
	γ-Proteobacteria	*Luteimonas mephitis*
		Nitrococcus mobilis
		Pseudoxanthomonas broegbernensis
		Vibrio alginolyticus
H_2S	*Firmicutes*	*Moraxella* sp.
		Acinetobacter sp.
		Exiguobacterium sp.
	β-Proteobacteria	*Thiobacillus thioparus*
		Thiobacillus sp.
		Thiothrix sp.
	γ-Proteobacteria	*Acidithiobacillus thiooxidans*
		Pseudomonas sp.
VOCs	*Actinobacteria*	*Rhodococcus erythropolis*
	Firmicutes	*Bacillus* sp.

found that the average removal efficiencies were 85.4%, 88.7%, and 89.0% for EBRTs of 30 s, 60 s, and 100 s, respectively (Chung et al. 1996; Elias et al. 2002; Cheng et al. 2010; Ilhem et al. 2011).

Febrisiantosa et al. suggested the different ventilation-biofilter methods for wastewater treatment, such as recirculating airflow ventilation system connected to a vertical biofilter (M1) and a plug-flow ventilation system connected to a horizontal biofilter (M2) (Febrisiantosa et al. 2020). They found that the M2 emitted lower concentration of odorous compounds than M1. Moreover, M2 could maintain the optimum temperature condition for a swine house during the cooler season. The plug-flow ventilation-horizontal biofilter system could be used for pig houses to minimize air pollution produced by swine farming activities and maintain optimum microclimate conditions for pigs. Acidic substances, which are produced during chlorinated volatile organic compounds, will corrode the commonly used packing materials and then affect the removal performance of biofiltration (Sven 2011; Martens et al. 2001).

5.2.2 Biotrickling Filtration (BTF) Reactors

Biotrickling filters (BTFs) have a similar structure to biofilters. The recirculation of the nutritional solution is the fundamental distinction between biofilters and biotrickling filters. In BTF, an aqueous liquid constantly drips over the filter bed, providing critical nutrients for microbial metabolism. Also, the BTF provides low bed pressure drop as compared to BF in the same condition. This leads to the lowest

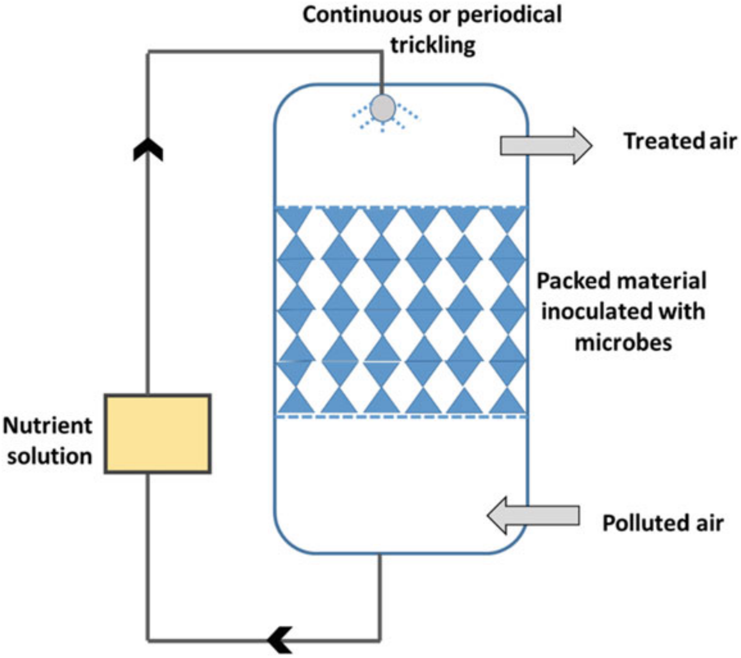

Fig. 5.3 A schematic representation of biotrickling filtration reactors

operating cost; therefore, BTF is considered the most suitable odor treatment in sewer systems. BTFs are widely used in the treatment of VOCs and odors. Compared to traditional compost or soil bed BFs, which are often confined to removing odorous compounds and nonchlorinated volatile organic compounds, BTFs can treat a broader spectrum of contaminants. A schematic representation of biotrickling filtration reactors is given in Fig. 5.3.

The working procedure of BTF is polluted gas enters the apparatus and flows in the same or opposite direction as the liquid phase, which absorbs pollutants. The film is constantly flooded with a liquid comprising nutrients and contaminants. Further, the biodegradation of pollutants takes place at the biofilm. After the pollutant has diffused across the liquid film, microorganisms and pollutants interact. As a result, the liquid flow rate and recycling rate have been identified as key characteristics for BTF operation. In a BTF, the packing medium has a great role in the pollutant degradation so that chemically inert materials are preferred. For bed preparation, chemically inert materials such as granular activated carbon, polymers, ceramic rings, glass balls, plastic structures, pebbles, and resins are commonly employed (Mudliar et al. 2010). The biodegradation of pollutants occurs in the biofilm formed through the growth of microorganism. Biofilms in biotrickling filters are often made up of more bacteria than fungi; bacteria such as *Pseudomonas*, *Bacillus*, *Staphylococcus*, and *Rhodococcus* are common in the BTF system. In numerous bioreactors used to eradicate H_2S and the number of VOCs, *Pseudomonas* has been identified as the superior species of the bacterial population. *Staphylococcus* has the ability to convert nitrate to nitrite; on the other hand, *Bacillus* can be found in both aerobic and denitrification environments; *Rhodococcus* is capable of degrading toxic environmental contaminants like naphthalene, toluene, herbicides, and other chemicals.

5.2.2.1 Factors Affecting the Performance of BTF

- **Empty Bed Residence Time** (EBRT): Increasing the EBRT is the simplest technique for BTF to boost removal efficiency (RE) (i.e., reducing the gas flow rate or enlarging the volume of packed bed). A lengthier EBRT can help both bulk transport of pollutants from the gas phase to the biofilm and biodegradation of pollutants in the biofilm. For example, Jia et al. reported that the RE of DMS increased from 74% to 97% for inlet concentrations of 6–27 ppmv (Jia et al. 2020). Also, the study of Chen et al. reported the RE of DMDS decreased from 100% to 50% at a fixed inlet concentration of 97 ppmv when EBRT decreased from 123 to 62 s for a maifanite-packed BTF (Chen et al. 2016).
- **pH and Temperature**: The microbial enzyme activity is highly influenced by pH and temperature; thus, the maintenance of optimal pH and temperature is very important. The ideal pH and temperature for most VSC-degrading microorganisms are 6–8 °C and 25–35 °C, respectively. Tu et al. found a BTF under acidic condition ($pH = 4$) mainly occupied by *Acidithiobacillus* had higher H_2S removal capacity compared with another BTF under neutral condition where *Thiobacillus* was the most abundant bacterial group (Tu et al. 2016). Another significant result was reported by Jia et al. who reported that when the pH dropped from 6.1 to 3.1 of the BTF containing *Bacillus*, *Hyphomicrobium*, *Pseudomonas*, and *Thiobacillus*, a decrease in the RE was observed for methyl mercaptan (10%) and dimethyl sulfide (24.7%) (Jia et al. 2020).

  Temperature can affect the activity of microbial enzymes, Henry's constants, and diffusion coefficients. In general, greater temperatures are linked to better enzyme activity and diffusion coefficients but reduced solubility, but extremely high temperatures can denaturize enzymes and cause them to lose their function. According to Shammay et al., the performance of BTFs affects badly the VSC removal during warm and dry conditions (Shammay et al. 2018).
- **Nutrients**: Nutrients are essential for the growth of microorganisms; thus, the supplement of nutrients is important. VSCs and CO_2 can be used as a sulfur and carbon source for microorganisms in general for BTF. Other essential nutrients such as nitrogen, phosphorus, potassium, calcium, sodium, and micronutrients are required for microbial activity and growth (Hayes et al. 2010). The results of Jaber et al. prove that the performance of BTFs for VSC removal improves when an extra source of nitrogen and phosphorus is provided to the reactor (Jaber et al. 2014). Also, the studies show that in BTF, while treating DMS with the addition of methanol in the inlet stream, the removal efficiency increased than the treatment without methanol (Zhang et al. 2006). However, the methanol concentration should be optimized because the inhibitory effect of methanol during the degradation process. Zhang et al. (2007) developed an optimized level of methanol

concentration for DMS removal and achieved removal efficiency 35% than in a BF.

- **Water Content and Trickling Operation**: Microorganisms require adequate water to maintain their metabolic activity; hence, the water content of packing materials is critical for BTF effectiveness. Depending on the packing materials used, the optimal water content of a biological filter is usually between 20% and 60% by weight. The poor saturation of incoming gas stream humidity and the exothermicity of pollutant biodegradation are the main causes of water loss in BTF, which therefore uses a continuous or intermittent trickling to compensate for the water loss. The trickling liquid velocity (TLV) is an important operating variable for BTF, and it is generally described as the circulating liquid flow rate divided by the filter bed's cross-sectional area. The overall mass transfer coefficient is affected by the varying TLV. The experimental result shows that as TLV increases, the overall mass transfer coefficient and bed pressure drop also increase. Furthermore, full-scale BTFs typically use intermittent trickling (IT), which helps with mass transfer and controlling excessive biomass growth. Furthermore, IT requires less maintenance, consumes little energy, and has a modest bed pressure decrease. Liu et al. investigated the effect of trickling liquid velocity (TLV) (0.02–6.1 m/h) on the mass transfer coefficients of VSCs for 11 types of packing materials and concluded the overall mass transfer coefficient and bed pressure drop increased with the TLV (Liu et al. 2015).
- **Packing Materials**: The packing material is the most important component of a BTF because it dictates its cost, performance, and longevity. The high surface area to facilitate microbial community colonization and high porosity to prevent a significant pressure drop are major properties affecting the packaging materials. Inorganic materials such as lava rock, CM-5 (a composite material mainly consisting of compost, calcium carbonate, perlite, cement, and plant fiber), cellular concrete, seashell, and UP20 (a nutritional synthetic material consisting of urea, calcium carbonate, phosphoric acid, and an organic binder) are used as packing materials, and their neutral pH maintenance favors microbial biodegradation of VSCs (Abraham et al. 2015). Organic packing materials, such as wood chips, pine barks, and compost, were also used in BTF (Jaber et al. 2014). Another significant packing material is the hybrid materials, for example, a BTF packed with hollow plastic balls in the upper layer and with lava rocks in the bottom layer; it is observed that the above hybrid packing enhanced the removal performance rather than the lava rocks alone (Tu et al. 2019).

BTFs frequently employed synthetic structured plastic media such as polyurethane foam and polypropylene ring. Large surface area, high porosity (90–98%), low weight, and chemical stability are some of their advantages. In addition, inorganic packing materials with acid buffer capability, such as lava rock, CM-5 (a composite material mostly composed of compost, calcium carbonate, perlite, cement, and plant fiber), cellular concrete, and seashell, were competitive options in BTF (Bu et al. 2021). BTF also employed organic packing materials such wood chips, pine barks, and compost (Jaber et al. 2014). These materials are low-cost, including ample nutrients and a great diversity of indigenous microbial species, as well as a high biomass concentration, despite the large pressure drop and short service time. Hybrid materials are another option for BTF to improve performance. When compared to a BTF packed only with lava rocks, a BTF packed with hollow plastic balls in the upper layer and lava rocks in the lower layer improved the removal effectiveness of dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) by 21–44% (Tu et al. 2019).

The biotrickling filter has the ability to react with acidic degradation entities of volatile organic chemicals, acidic or alkaline compounds, and acidic odorous gases, as well as having low operating and capital expenses and a lower pressure decrease over time (Lebrero et al. 2012). As a result, when this advantage is combined with its cost-effectiveness, the biotrickling filter technology could be an outstanding solution for controlling VOCs and odor emissions from various industrial processes.

On the other hand, during the operation of biotrickling filters, the drawbacks may include excessive growth of biomass in the bed, which can lead to clogging and, as a result, a decrease in efficiency (Alonso et al. 2001). However, there are effective methods to counteract this, such as temporarily increasing the flow of the liquid phase, which will result in breaking a part of the biofilm from the filling (Smith et al. 1996), or by using the right microorganisms to remove excess bacterial biofilm (including protozoa), or by using the right chemical to damage part of the bacterial biofilm (Cox and Deshusses 1998).

5.2.3 Bioscrubber Reactors

A bioscrubber is a biofilter combined with a wet scrubber that preconditions the waste gas by removing dust and lowering the inlet temperature. It is possible to distinguish two types of bioscrubber “fixed film bioscrubber (biotrickling filter)” and “suspended growth bioscrubber (bioscrubber).” Both the systems work similarly as they use microorganisms, media, and water. In bioscrubber, treatment systems rely on microorganisms present in water that is recirculated through treatment vessel, whereas in biotrickling, water will not be recirculated and microorganisms grow within the media (Waweru et al. 2006; Singh et al. 2005).

Bioscrubbers are safer system than other odor treatment devices such as incinerators and chemical scrubbers because no hazardous chemicals are required and danger from fire hazard is remote. Sustainability is a hallmark of biological odor control systems, avoiding transport, storage, and off-gassing of chemicals, media replacement, and material disposal issues. Developments in bioscrubber technology led to significant progress in the removal of difficult to degrade odorous compounds emitted from industrial and municipal wastewater treatment (Soyoung et al. 2022).

5.2.3.1 Bioscrubber Operation Principle

Bioscrubbing consists of the physical separation or absorption of odors in the liquid phase in an absorber unit, followed by the biological treatment in a liquid-phase bioreactor (Krzysztof et al. 2017; Turgeon et al. 2009). By recycling the effluent from the bioreactor to the top of the absorber unit, efficient gas cleaning of highly soluble pollutants is ensured. The removal of odorous compounds in bioscrubber involves absorption of odorous compounds from the gas phase to the aqueous phase and biodegradation of the pollutants contained in the aqueous phase by the active microorganisms present in the bioreactor. These microorganisms can be either heterotrophic (need a source of organic carbon to provide both energy and carbon for cell growth and synthesis) or autotrophic (get carbon from carbon dioxide in the air stream, and oxidation of sulfide to either sulfate or elemental sulfur provides cellular energy for growth and respiration) (Valero et al. 2019; Van Groenestijn 2001).

The absorber unit provides gas-liquid contact under conditions favoring mass transfer of pollutants from the gas phase to the extended surface area of the aqueous medium. Packed tower and spray tower absorbers are most suitable for bioscrubbing, as the elimination efficiencies for less water-soluble pollutants in other absorber designs are lower. The bioreactor unit degrades the pollutant contained in the aqueous effluent from the absorber. Under continuous aeration, the pollutant is converted by the active microorganisms into CO_2, H_2O, and biomass. Bubble size is an important factor in supplying air to the bioreactor. Reduction of H_2S odors in fine-bubble diffusers can be higher than in coarse-bubble diffusers. The bioreactor effluent (absorber medium) is recycled and reused in the absorber. The operation principle and design of bioreactors for bioscrubbing are similar to those of the activated sludge tanks used in wastewater treatment plants (Bravo et al. 2017; Potivichayanon et al. 2006) (Fig. 5.4).

The main design parameters for bioscrubbers are the media type, air detention time, and liquid flow rate and quality. The latter can be controlled by the ratio of recirculation flow rate to makeup water flow rate. The ratio is used to directly modify

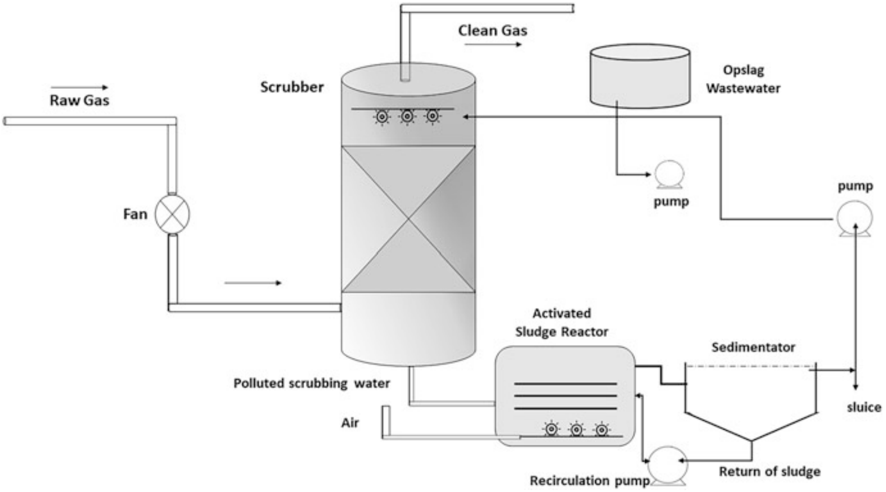

Fig. 5.4 Schematic representation of bioscrubbers

pH and food supply input, indirectly impacting biomass, microbial population, and resultant odor control capability. Media types that have been used successfully include lava rock, plastic cross-flow, plastic random dump, and foam. Foam media have typically been used in short detention time, high velocity, and high pressure drop bioscrubbers directed primarily at hydrogen sulfide control. Plastic or rock media are found in longer detention time systems at lower pressure drop and aimed at control of both H_2S and organic odorous compounds. It is generally acknowledged that longer detention time is required for control of organic odorous compounds or for a high level of hydrogen sulfide control. Secondary effluent is typically used either as makeup water or applied in a once-through mode. The effluent provides the food supply and nutrients to encourage biomass growth as well as enable control of pH in the bioscrubber (Singh et al. 2005; Malhautier et al. 2003).

5.2.3.2 Applications of Bioscrubbers

Compared to a conventional biofilter or biotrickling filter, the bioscrubber offers the significant advantage of producing and sustaining much larger amounts of microbial biomass in more compact process units while maintaining very high specific substrate utilization rates (Singh et al. 2005). Most existing bioscrubbers are designed for the removal of a single pollutant. In order to increase removal efficiency or to improve operational flexibility in handling pollutant mixtures, various design modifications such as sorptive-slurry bioscrubber, anoxic bioscrubber, two-liquid phase bioscrubber, airlift bioscrubber, spray column bioscrubber, or two-stage bioscrubber have been considered (Nurul Islam et al. 1998; Lalanne et al. 2008).

For the removal of sulfur-containing odorous compounds that are difficult to degrade, the choice of microorganisms is of key importance. Immobilized cells of *Chlorobium limicola* can transform H_2S into elemental sulfur in an autotrophic reaction, and heterotrophic *Xanthomonas* species are also known to remove H_2S from gas streams. Efficient degradation of sulfur-containing compounds by certain strains of *Thiobacillus* and *Hyphomicrobium* has also been reported. The pH value of 8.5–9.0 is the optimal range that facilitates maintaining a high biological activity and, at the same time, ensuring effective absorption of H_2S. Similar to pH, the temperature is also known to be very important for microbial activity. In the temperature range of 25–35 °C, the efficiency of sulfide oxidation by *Thiobacillus denitrificans* is highest, but below 16 °C, it is significantly reduced (Akanit et al. 2021; Sa'adah et al. 2022).

Bioscrubbers have application in various industries such as odor detection in the cigarette industry (odor concentration is reduced by approximately 5000 ou/m^3 to 200–300 ou/m^3), removal of odor and sulfur components from flue gases in the rubber industry and in the production of methionine, and removal of odor arising from the production of aromas, enzymes, polymers, etc. Bioscrubber is the best technique to remove odor components such as NH_3 and H_2S from gas originating from water purification plants, which is also used to remove hydrocarbon and nitrogen components during the processing of paint residues (Nisola et al. 2009; Potivichayanon et al. 2006; Hartung et al. 2011).

Bioscrubbers are undoubtedly one of the simplest odor control systems to operate. Instrumentation is minimal, normally limited to level control, a liquid flow meter, and a pH meter, typically with two control loops. The bioscrubber technology offers operational stability and effective control of operating parameters such as pH and nutrient dosage, relatively low gas pressure drop, and small space requirement. Compared to biotrickling filtration, the risk of clogging of the packing material by growing biomass is avoided. Large gas flow rates and high pollutant concentrations can be handled; moreover, as reaction products are removed by washing, concentrations of toxic by-products generated in the reactor can be maintained at low levels. The possible disadvantages of bioscrubbers are the generation of liquid waste and the risk for excess sludge generation, as well as the slowest growing microorganisms being washed out. Furthermore, as the residence time of gaseous pollutants in the absorption unit is short, bioscrubbing is less suitable for less water-soluble compounds. It was found that bioscrubber applications can be cost-effective for pollutants with a dimensionless Henry's coefficient of the order 0.01 (Singh et al. 2005; Waweru et al. 2006).

5.2.4 Membrane-Based Reactors (MBRs)

With the intention of biological treatment of sewage produced from a manufacturing plant, Smith et al. in 1969 introduced the MBR technology during the Dorr-Oliver research program. High energy costs and membrane fouling restricted the broad applicability of this technique. In 1989, Yamamoto et al. resolved these obstacles through an innovative configuration by placing the hollow fiber membrane in the activated sludge aeration tank (Al-Asheh et al. 2021) and also made changes such as instead of using a pressurized pump installed outside to circulate the mixed liquor across the membrane, suction pressure was applied into the bioreactor where the membrane immersed directly inside the aeration tank. In the mid-1990, after the introduction of immersed configuration, a number of studies have been applied to increase the application of MBR technology with reduced cost. After 2008, the usage of MBR plants was initiated worldwide for sewage water treatments. According to the recent BCC (Business Communication Company) report, MBR's market size is 3.0 billion USD in 2019 and is expected, at a compound annual growth rate (CAGR) of 7%, to reach 4.2 billion USD by 2024 (Al-Asheh et al. 2021).

Membrane bioreactor (MBR) is a new type of biological treatment technology; it combines the biological process with membrane filtration called membrane bioreactor (MBR). It acts as an alternative to traditional bioreactors for waste gas treatment. The membrane bioreactor has a pore size of 0.1 μm, which allows the selective permeation of the pollutant, which is the main difference from other reactors. Membrane filtration ensures that microorganisms are completely trapped in the bioreactor. This gives better control over the biological reactions and modifies the conditions of the microorganisms in the aerated tank, which makes a long sludge retention time (SRT) and high mixed liquor suspended solid (MLSS) concentration. MBR is widely used for municipal and industrial wastewater treatment. But the fouling phenomenon is the main obstacle for membrane-based reactors. Generally, the MBR process can be divided into three categories according to the working mechanism: rejection MBR, extractive MBR, and diffusive MBR. However, most reports are based on wastewater treatments and are rejection-based MBR processes; other two types are under developing stage. A schematic representation of MBR is given in Fig. 5.5.

The conventional biofiltering methods have limitations in certain conditions such as at high VOC loading rates, microbial growth results in plugging of pore spaces in biofilters with microbial biomass. Ultimately, the systems fail due to high head losses across the media. Biofilters also face limitation during the formation of acidic metabolites resulting in acidification of the biofilter media, such as in the degradation of the chlorinated hydrocarbon, dichloromethane. In order to avoid this limitation,

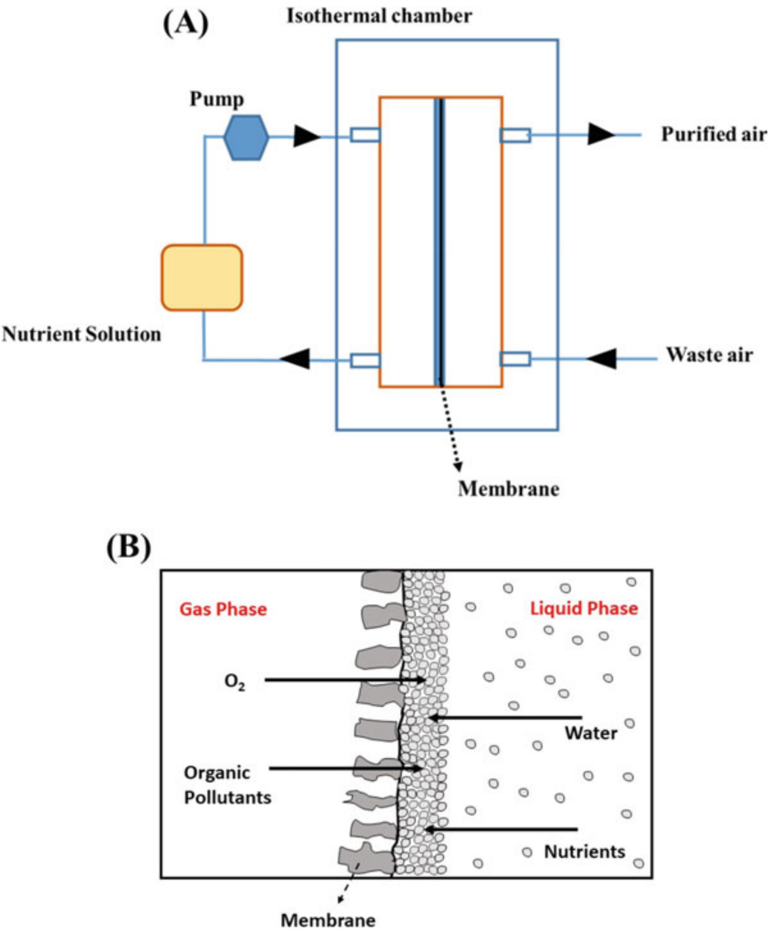

Fig. 5.5 (**a**) Schematic representation of membrane-based bioreactor. (**b**) Schematic representation of membrane (Mudliar et al. 2010)

Ergas et al. introduced hollow fiber membrane bioreactors for the treatment of VOCs. The authors designed a membrane-based treatment technology in lab scale for toluene (Ergas and McGrath 1997), and they attained 98% of removal of toluene at an inlet concentration of 100 ppmv. A novel extractive membrane bioreactor (EMB) system was introduced by Freitas dos Santos et al. for the treatment of contaminated gas streams. The authors used a silicone rubber membrane for the treatment of 1,2-dichloroethane (DCE) (Freitas Santos et al. 1995). Comparison of the EMB to a direct bioscrubbing process showed that the EMB system has superior volumetric efficiency. The EMB, with 2.5 m^2 of membrane surface contained in a spirally wound module, degraded 91% of the DCE. In a recent report, the authors made an effort to prove the efficiency of MBRs for the treatment of water-soluble and moderately soluble VOCs (Lebrero et al. 2013); the analysis of acetone, toluene, limonene, and hexane at trace level concentrations with different gas residence times (GRT) of 60, 30, 15, and 7 s was demonstrated. The results show high acetone and toluene removals (>93%), but a maximum removal of 2% was observed for hexane. However, the maximum percentage of removal of limonene was observed.

5.2.4.1 Mechanism of Membrane-Based Biological Waste Gas Treatment

Mass transfer and the microbial kinetics of gaseous pollutant is the main mechanism of membrane-based reactors. The driving force of mass transfer is the concentration difference of gas phase and biofilm phase. This driving force depends strongly on the air-water partition coefficient of the diffusing volatile components, and for a component having a high partition coefficient, the driving force for mass transfer is small. The mass transfer and microbial kinetics of a gaseous pollutant within a membrane bioreactor for waste gas (MBRWG) module can be described by bulk mixing of contaminants entering to the bioreactor followed by the air boundary layer transport (Kumar et al. 2008). The pollutant transfers to the biofilm through its dissolution and diffusion property with the biofilm material. However, the diffused pollutants undergo degradation within the biofilm, and the boundary layer transport will be through the liquid phase.

The main advantage of MBR over BF is the presence of a discrete water phase that creates optimal humidification of the biomass and removal of the degradation products, thus avoiding inactivation of the biomass. In the case of MBR, the membrane serves as the interface between the gas phase and the liquid phase. This gas-liquid interface thus created is higher than in other types of gas-liquid contactors, and the large gas-liquid interfaces allow high mass transfer rates.

5.2.4.2 Membrane Materials

Two types of membrane materials have been used to prevent mixing the gas and liquid phases and simultaneous transfer of volatile components. They are hydrophobic microporous membranes and dense membranes (Mudliar et al. 2010).

1. ***Microporous membranes***: Microporous membranes are highly porous, a commercial type of membrane having 30–85% pore space. The surface pores are generally submicrometer in size. If the size is large, it allows organisms through

the membrane, and then intrusion by organisms and organics will occur, which reduces mass transfer, potentially plugging the gas phase. Thus, control of pore size is significant in the membrane. Commonly polymer-based membranes are used for wastewater treatment. Polysulfones (PSFs) and polyvinylidene difluoride (PVDF) are famous for their long-lasting properties. In recent times, polytetrafluoroethylene (PTFE) and cellulose acetate (CA) have been used for the membrane materials (Mudliar et al. 2010).

2. ***Dense membranes***: A dense-phase membrane has no pores, but contaminants such as volatiles are adsorbed on the surface and diffused through the dense membrane (Mudliar et al. 2010). Also, the mass transfer coefficient of the dense membrane depends on the solubility and the diffusivity of the volatile component in the dense matrix. The solubility and diffusivity for each volatile component are different. Their mass transfer resistance with dense membranes also varies; the main reason for this variation is the specific interactions between the components in the gas phase and the membrane material. This gave an advantage such as components can be selectively extracted from or retained in the gas phase by a proper choice of the membrane material.

5.2.4.3 Membrane Fabrication Methods

The major membrane manufacturing processes are non-solvent induced phase separation (NIPS), melt-spinning and cold-stretching (MSCS), and thermally induced phase separation (TIPS) (Al-Asheh et al. 2021).

1. ***Non-solvent Induced Phase Separation (NIPS)***: In this method, the membrane is fabricated due to the solubility difference of polymers in different solvents. In this fabrication process, in the beginning, the polymer is mixed with the highly soluble solvent. Then the prepared solution is added to the weakly soluble solvent with the aid of injection nozzle so that the highly soluble solvent permeates into the poor solvent; as a result, hardening (gelation) will occur, and also the diffusion of solvent creates pores on the membrane.
2. ***Melt-Spinning and Cold-Stretching (MSCS):*** This process involves, initially, the melting of polymer and then cooling it down just under the melting temperature while simultaneously applying stretching in one or two directions. Through this process, crystalline morphology will remain the same, while the amorphous structure is lengthened and creates a wide range of pore sizes. The MSCS method is the cheapest membrane preparation even though the formation of uncontrolled pore size acts as a significant disadvantage of this process.
3. ***Thermally Induced Phase Separation (TIPS)***: This method has an intermediate step between the previous two methods. In this method, polymers are dissolved or diluted at high temperatures followed by rapid cooling in cold liquid to remove all the remaining solvents. In order to improve the mechanical strength of the membrane, stretching process is applied. The primary issue related to this process is the weakness of the fabricated membrane.

5.2.4.4 Issues Related to the MBR Separation Process

Membrane fouling is the main issue faced in the MBR-based separation process (Al-Asheh et al. 2021). Thus, the efficiency of the MBR process depends on how to manage or fix the fouling issues during operation. The factors that influence the membrane fouling are operating conditions, membrane cleaning strategies, characteristics of wastewater influent, and membrane properties. Many lab-scale and pilot plant-scale fouling control experiments have been examined for a long time to resolve this problem. From these investigations, different strategies such as pretreatment, substrate modification, membrane surface modification, optimization of operating conditions, and physical or chemical cleaning methods are formulated to control the fouling of the membrane. Another significant disadvantage of the MBR process is the higher capital and operational cost because the membrane is expensive; also, the maintenance and antifouling strategies are costly to process. Also, the greater aeration demand of MBR tends to produce high foaming, and finally, the MBR operation requires high power consumption.

5.2.4.5 Types of MBR and Novel Configurations

Aerobic and Anaerobic Membrane Bioreactor (AnMBR)

Aerobic technology is the most commonly used technique to treat wastewater and effluents from industries. The aerobic process is used for the treatment of effluent with biodegradable chemical oxygen demand (COD) content lower than 1000 mg/L. On the other hand, an anaerobic technique is used to treat highly polluted effluent, where the biodegradable COD content is over 4000 mg/L. The anaerobic process has various advantages, such as the production of renewable fuel by the decomposition of organic matter present in the wastewater, the retrieval of water by treating wastewater, and the recovery of nutrients for the generation of agricultural fertilizers.

The incorporation of anaerobic digestion treatment with membrane filtration led to the development of an alternative MBR configuration to overcome the obstacles of MBR processes (Maaz et al. 2019). Because of the anaerobic digestion treatment system, the energy requirement of wastewater treatment is reduced due to the production of methane-rich biogas from the decomposition of organic matter. Also, it helps to recover the nutrients through the conversion of nutrients into chemically available forms. However, membrane stability, membrane fouling, dilute resources, and salinity buildup are some of the main hurdles that need to be resolved in the development of AnMBR. The two parts of the AnMBR plant are the anaerobic bioreactor and membrane models. In terms of bioreactor configurations, upflow anaerobic sludge blanket (UASB), completely stirred tank reactor (CSTR), and anaerobic fluidized bed bioreactor (AFBR) are the most frequent ones for AnMBR. The CSTR is the most common structure used in AnMBR due to its simple operating and construction process. The membrane models can be integrated with an anaerobic bioreactor in three different ways: (a) side-stream AnMBR, where membrane module is located outside the bioreactor tank; (b) internally submerged AnMBR, submerging membrane inside the bioreactor tank; and (c) externally submerged AnMBR, where the membrane unit is immersed in a different chamber from the working bioreactor. Externally submerged configuration is used mainly in pilot-scale applications and showed great potential in large-scale domestic wastewater treatment. Lower energy demand for pilot-scale externally submerged AnMBR configuration (commonly hollow fiber membranes were used) compared to lab-scale AnMBR and aerobic MBRs was reported. Huang et al. reported a pilot-scale anaerobic membrane bioreactor for pharmaceutical wastewater treatment (Huang et al. 2018). Their study focused on the removal of β-lactam antibiotics (BLAs), including amoxicillin, ceftriaxone, cefoperazone, and ampicillin, from real samples. The authors claimed the highest removal efficiencies for amoxicillin, ceftriaxone, cefoperazone, and ampicillin were 73.2 ± 4.3%, 47.7 ± 2.2%, 79.4 ± 4.1%, and 34.6 ± 3.3%, respectively. Also, the authors reported a total COD removal efficiency of 94.0%.

Anaerobic Fluidized Membrane Bioreactor (AFMBR)

Membrane fouling is one of the challenges faced by AnMBRs, despite many advantages like removing antibiotics. Hence, AFMB has been recently developed to reduce the cake layer formation rate and simultaneously increase the removal of antibiotics from wastewater. It is a combination of membrane technology and circulation of liquid and sprinkle of particles. AFMB has many advantages over AnMBR, such as increased antibiotic removal, reduced extracellular polymeric substances, soluble microbial product concentration, and more stable sludge with higher size. More studies are required to understand the performance of this novel model (Guoa et al. 2020). It is reported that the addition of carriers could decrease the energy needed for the performance of AFMBR compared to AnMBR. The study of Kim et al. demonstrated the feasibility of polymeric media with a tubular shape consisting of polyvinylidene fluoride as fluidizing agent for anaerobic fluidized bed membrane bioreactor (AFMBR) for the treatment of synthetic wastewater (Kim et al. 2020). The authors reported that the new method provides 87.6% of chemical oxygen demand (COD) removal, which yields 10 mg/L of COD in membrane permeate. Also, the long-term reactor operation showed an excellent organic removal efficiency higher than 90% during the operational period. The low energy consumption and excellent biofilm formation are other important advantages of this new approach.

Membrane Photobioreactor (MPBR)

MPBRs are typically made up of various submerged micro- or ultrafiltration membranes, such as hollow fibers or flat sheets combined with PBRs. MPBR has several advantages, including effective microalgae separation, system stability, and improved effluent quality. But this type of configuration is inefficient to treat primary raw domestic wastewater containing high organic matters. This inefficiency arises due to the inadequate amount of organic matter that can be used as a food source for microalgae and help them grow to treat wastewater (Guoa et al. 2020). The effects of various parameters on MPBR performance, such as hydraulic residence time (HRT) and organic loading rate (OLR), have been investigated. According to recent studies (Ashadullah et al. 2021), the system does not require any external aeration source and can effectively create microalgal biomass and simultaneously remove organics and nutrients. In a recent report, Wu et al. put forwarded a novel polyvinylpyrrolidone (PVP)-graphene oxide (GO)/PVDF hollow fiber membrane with attractive antifouling characteristics (Wu et al. 2020). Furthermore, the authors demonstrated the treatment of ammonia nitrogen wastewater by using PVP-GO/PVDF membrane applied into algae-membrane photobioreactor (MPBR). The novel PVP-GO/PVDF membrane exhibited improved hydrophilicity (contact angle decreased from 97° to 62°), better permeability (1.7 times), and attractive flux recovery rate (96%) in MPBR filtration.

Membrane Bioreactor Integrated with Microbial Fuel Cell (MFC-MBR)

One of the major issues preventing MBR from being widely used is fouling. It has been demonstrated that applying an electric field to MBR reduces foulant deposition on the membrane surface, resulting in a reduction in fouling phenomena. Recently, a novel configuration has been developed by the integration of MFCs with MBRs (Yin et al. 2020). In this configuration, applying direct electricity to MBR is eliminated by the consumption of electricity produced by MFCs. Thus, the total energy requirement for the process will be reduced; also, the performance of the bacteria is not affected due to high electric fields. Tian et al. developed a novel microbial fuel cell-membrane bioreactor in this system; a maximum power density of 2.18 W/m^3 and an average voltage output of 0.15 V were achieved at an external resistance of 50 Ω (Tian et al. 2015). The removal efficiencies of COD, ammonia nitrogen, and total nitrogen (TN) in the MFC-MBR were improved by 4.4%, 1.2%, and 10.3%, respectively. An efficient energy recovery was observed in the MFC-MBR. The average voltage and maximum power production of the MFC-MBR were 0.15 V and 2.18 W/m^3, respectively. Four remarkable effects of the MFC integration on sludge properties, including less loosely bound extracellular polymeric substance (LB-EPS) reduction, increased ratio of protein in soluble microbial products (SMP_p) and carbohydrates in soluble microbial products (SMP_c), floc size homogenization, and filamentous bacterial growth inhibition, were achieved in the MFC-MBR. With these effects, dewaterability and filterability of the sludge in the MFC-MBR were improved.

Li et al. (2021) investigated the fouling characteristics of sludge in MFC-MBR by immersing anodic and cathodic chambers of MFC in aerobic MBR using a hollow fiber membrane. The fouling process was studied using the extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) model. The results showed that the free energy of adhesion between the SMPs and the clean membrane or the SPM-fouled membrane is lower in MFC-MBR than in control systems (C-MBR). The authors also concluded that the SMPs in MFC-MBR face higher energy barriers to be absorbed on the membrane surface, which inhibits adsorption; as a result, fouling can be reduced. Another advantage of this configuration is that sludge flocs in MFC-MBR have lower hydrophobicity and a lower negative surface charge.

Numerous studies have been conducted to analyze the performance of different configurations of MBRs to treat various types of wastewater as their feedstock, either synthesized wastewater or real industrial ones. Their performance was evaluated in terms of COD removal percentage, membrane fouling propensity, biogas production, and, finally, maximum power and current density generation. Several studies have been conducted at various levels to assess the potential of the proposed configuration at the industrial level. As a result, the efficiency of MBRs was calculated in both pilot and lab scales under various operating conditions.

5.2.5 Other Bioreactor Configurations

5.2.5.1 Rotating Drum BF

Yang et al. (2002) proposed an innovative design that consists of a rotating drum BF. In this new design, open-pore reticulated polyurethane is used as the packing medium. Also, the design results in better distribution of VOCs, oxygen, nutrients, and biomass than the conventional BFs. To investigate the effect of medium configuration on VOC treatment, the performances of the two types of rotating drum BFs were examined. One was a single-layer BF that consisted of a thick layer of open-pore reticulated polyurethane foam media. The other was a multilayer BF that used a set of four concentric thinner layers of the media. The two different media configurations were examined through the investigation of diethyl ether at various organic loading rates. The results show the stability and higher ether removal efficiency of multilayer BF than that of the single-layer BF. Also, the multilayer BF exhibits more biomass distribution on the concentric surface than the single-layer BF, resulting in a reduced possibility of short circuiting of gas streams and better performance.

5.2.5.2 Rotating Rope Bioreactor (RRB)

Mudliar et al. (2008a, b) introduced another novel rotating rope bioreactor (RRB) to treat highly volatile and water-soluble VOCs. Also, the reactor could be used to treat vapor-phase VOCs by properly scrubbing the compound in water and treating it into the rotating rope bioreactor. This new bioreactor provided higher interfacial area (per unit reactor liquid volume) along with increased oxygen mass transfer rate, excellent microbial culture stability, higher substrate loadings, and better removal rates compared to the conventional biofilter reactors. The authors demonstrated the efficiency of RRB through the removal treatment of wastewater containing pyridine, and the experimental result shows more than 80% of removal efficiency. Further, the authors also described a single-stage reactor called the rotating rope biofilter for direct VOC treatment instead of a two-stage process. This reactor is a modified closed RRB where the waste air containing the VOC is passed through the water holdup of the reactor. Further, the absorption of water-soluble VOCs will take place in the aqueous phase. Afterward, the degradation of VOCs occurs through the immobilized microbes on RRB rope media.

5.2.5.3 Foamed Emulsion Bioreactor

Kan and Deshusses (2003) designed a new bioreactor called foamed emulsion bioreactor (FEBR) for air pollution control. The new reactor was based on an organic-phase emulsion and actively growing pollutant-degrading microorganisms, made into a foam with the treated airflow. The FEBR does not expose to clogging even though there is no packing in the reactor. The mathematical modeling of the process and the proof of a laboratory prototype revealed that the FEBR shows excellent performance than other gas-phase bioreactors. From the experimental results, the toluene removal efficiency found was 95%.

5.2.5.4 Rotating Biological Contactors

Rotating biological contactors (RBCs) are aerobic biological wastewater treatment units; they are also known as rotating biological filters or rotating disk contractors. The first RBC was developed during the 1920s; however, in the 1960s onward, the commercialization of RBC was initiated in West Germany. After that, its wide application was initiated around the globe. RBC technique was initially developed for wastewater treatment applications and later developed for waste gas purification (Mba 2003). In biofilters or biotrickling filters, the biodegradation of pollutants occurs in stationary biofilms, wherein RBC polluted air is brought into contact with biofilm attached to a rotating surface. The primary type of RBC is rotating drum biofilter (RDB), in which a closed chamber contains reactor disks (also called medium support) mounted on a rotating shaft, covered with sponge medium, and partly dipped in the aqueous nutrient solution. The rotational movement of the disks favors mass transfer and controls the growth of film on the medium-covered disk surfaces. Polluted air can flow to/from the filter chamber directly or through channels in the hollow shaft. The advantage of all these systems is that they are compact (i.e., in densely populated urban settings) and efficiently reduce organic matter. However, this technique requires experienced staff for construction operation and maintenance. Several reports of rotating biological contractors to remove odorous gases are available mainly for VOCs. The experimental result of Padhi and Gokhale (2016) shows that RDB application with a sponge as supporting media can remove gaseous benzene and their results show 95% removal efficiency.

5.2.5.5 Two-Phase Partitioning Bioreactors

The two-phase partitioning bioreactors (TPPBs) emerged in the early 1990s as innovative multiphase systems capable of overcoming some of the key limitations of traditional biological technologies such as the low mass transfer rates of hydrophobic VOCs and microbial inhibition at high VOC loading rates. TPPBs differ from the other bioreactors because instead of a single liquid (aqueous) phase, two immiscible liquid phases are employed in TPPBs (Muñoz et al. 2012). The aqueous phase supports biological activity through nutrient supply, and the non-aqueous phase (NAP, e.g., hexadecane or silicone oil) enhances the hydrophobic pollutant transfer to biodegrading microorganisms. The non-aqueous phase (NAP) could be the base of TPPBs, which shows good affinity toward the target VOC; as a result, VOC absorption increases, and it acts as a driving force for mass transfer. The reactor configuration and the presence of NAP improve the hydrodynamic behavior of the bioreactor; therefore, the interfacial area of both gas/water and a gas/NAP gets increased, which enhances the VOC mass transfer rate. NAP also buffers process microbiology against the stream of VOCs by temporarily decreasing the VOC concentration in the aqueous phase or acting as a VOC reservoir, which ultimately results in an enhanced process. Most NAP liquids used in the TPPBs also have an affinity to oxygen, further enhancing pollutant removal. The major factors that influence the performance of a TPPB are (1) the selection of the NAP, (2) the type of microbial community, and (3) the reactor configuration. The selection of NAP liquid depends on the characteristics of pollutants (type, flow rate, concentration) and the kind of microbial community; in addition to that, the biocompatibility, non-biodegradability, low emulsion-forming tendency, non-toxicity, low vapor pressure, low viscosity, and density different from water were also required for the NMP selection.

There are certain coupled or combined bioreactors to improve the efficiency of the conventional bioreactors. Liu et al. (2020a, b) demonstrate a full-scale combined bioreactor with a biological aeration zone (BAZ) and a biological filtration zone (BFZ) for the treatment of odorous compounds, VOCs, and aerosols emitted from a landfill site. Their experiment reveals that the combined system shows an average removal efficiency (RE) of 97.21% for H_2S, 98.89% for NH_3, 92.44% for VOCs, 73.12% for cultured bacteria, and 81.89% for fungi. The authors also claimed that the combined bioreactor is low-cost and effective for odorous and volatile organic compounds. Anaerobic digestion with thermal hydrolysis (THP-AD) is another effective sludge treatment method that provides several advantages, such as enhanced biogas formation and fertilizer production. The main limitation to THP-AD is that hazardous odors, including NH_3 and volatile sulfur compounds.

Another important degradation technique is plasma technology, which is already used in various applications such as surface treatment, surface coating, reforming of carbon dioxide and methane, removal of volatile organic compounds, odor abatement, and disinfection (Dobslaw and Glocker 2020). Majorly non-thermal plasma and thermal plasma were used for the treatments; recently, steam plasmas were established. Among these plasma technologies, non-thermal plasma in modular form was built with the combination of a mineral adsorber and bioscrubber for abatement of volatile organic components (VOCs). Thermal plasmas are usually arc-heated plasmas operated with different plasma gases such as nitrogen, oxygen, argon, or air. The steam plasmas were generated by adding liquid water as plasma gas. However, these technologies have certain hurdles to resolve, such as previous reports are based on lab-scale and pilot plant-scale operations. Still, proper scale-up technologies were not established. Also, the lab-scale experiments were focused on a particular pollutant, but mixed VOCs and their interference need to be investigated. Finally, the energy demand for the process needs to be reduced.

5.3 Conclusion

The studies reveal that both anthropogenic activities and natural processes cause the generation of harmful VOCs and odorous compounds. Therefore, the development of treatment technologies is essential for a pollution-free environment. It is well known that physiochemical treatment methods such as ozone, UV rays, and non-thermal plasma show high efficiency, but these methods are more expensive and high energy-consuming than biological methods. Literature has demonstrated that biological methods of odor removal give high effects of bio-purification of the air, up to 95–99%; moreover, their advantage is manifested primarily in the economic aspect and in terms of environmental friendliness. Many research groups reported appreciable removal efficiency through biological processes in lab scale to a maximum of pilot plant scale. However, the wide application of bioreactors in real conditions such as industrial plants, waste management plants, and municipal and industrial wastewater treatment plants faces certain hurdles during the treatments. Therefore, it is essential to study the influence of the parameters of the bio-treatment process and external conditions of bulk treatments, which will differ from the lab-scale treatments. The biological treatment technologies are limited in the abatement of the mixture of greenhouse gases (GHGs) and a mixture of VOCs; therefore, it is necessary to implement advanced techniques in the existing procedure so that time and cost for new treatment methods can be avoided. The cost-effective and eco-friendly approach always prefers biological treatment in the first place in bulk treatments; thus, the establishment of biological treatment on a bulk scale is necessary.

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Biological Treatment of Endocrine-Disrupting Chemicals (EDCs)

6

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Abstract

Endocrine-disrupting chemicals (EDCs) such as natural estrogens, bisphenol A, and nonylphenol are widely spread in the environment due to improper waste disposal. Emergence of EDCs mainly occurs from widely used consumer

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products like pharmaceuticals, personal care products, plastic preservatives, pesticides, and industrial lubricants. Both acute and chronic exposure of EDCs may influence the endocrine system of organisms arising severe health issues, thereby ultimately resulting in an imbalanced ecosystem. Degradation of EDCs has been largely studied in flocculation, precipitation, adsorption, and chemical oxidation-based wastewater treatment systems. Bioremediation of EDCs by a diverse range of taxonomical group's microorganisms provides several advantages through economically adequate environmental protection. Microbial strains such as bacteria, microalgae, and fungi participate in the biodegradation and biotransformation processes of EDCs making them less endocrine-disrupting or harmful. Using various enzymes, microorganisms degrade complex EDCs into simple compounds or end products such as CO_2 and H_2O during their metabolic process. Fungi are the most widely used microorganism taxa for the degradation of a wide variety of EDCs. This chapter provides an overview of sources, pathways, and fate of EDCs in the environment and novel biodegradation approaches. Finally, future directions are identified in terms of unrevealed degradation mechanisms and field applications.

Keywords

Endocrine disrupters · Bioremediation · Microbial strains · Bioaccumulation

6.1 Introduction

6.1.1 Endocrine-Disrupting Chemicals

It is essential to have consistent communication among the various organs in the organisms to respond to every change of the internal and external environment. The human body contains two major information transmission systems: the nervous and endocrine systems (Hiller-Sturmhöfel and Bartke 1998). Both systems play a vital role in integrating, coordinating, and responding to sensory information while maintaining the relative stability of the body's internal environment. The endocrine system releases hormones inside the body to regulate various functions such as metabolism, growth and development, emotions and mood, fertility and sexual activities, sleeping, and blood pressure. Any disorder or malfunction of the endocrine system may cause various health effects resulting in altered normal hormonal functions. Some natural and synthetic compounds in the environment, food, and consumer products can adversely affect the endocrine system, and they are called endocrine-disrupting chemicals or compounds (EDCs) (Diamanti-Kandarakis et al. 2009; Kudłak et al. 2015). According to the World Health Organization (WHO), "An endocrine disruptor is an exogenous substance or mixture that alters function (s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub)populations"; and "A potential endocrine disruptor is an exogenous substance or mixture that possesses properties that might be expressed to lead to endocrine disruption in an intact organism, or its progeny, or (sub)populations" (WHO 2013). By altering the hormone synthesis, release, storage, metabolism, and transport processes, EDCs can remove or bind endogenous hormone receptors. The United Nations has published a list of 45 chemicals that have been recognized as EDCs in 2018. The list includes 17 categories of EDCs, and some of them are 4-nonylphenol, 4-*tert*-octylphenol, 4-heptylphenol, 4-*tert*-pentylphenol, phthalates, benzophenone, butylated hydroxytoluene, parabens, carbon disulfides, tebuconazole, triclosan, etc. (Chemsafetypro 2018).

6.1.2 Sources of ECDs in the Environment

Many EDCs are directly discharged to the environment from different sources such as industrial waste effluents and fumes, hospital waste effluents, livestock, municipal waste, sewage treatment plants, and domestic waste (Fig. 6.1). Most chemicals recognized as EDCs are heterogeneous and synthetic. Different types of EDCs can be found from domestic and industrial sources, and they are summarized in Table 6.1. The emergence of EDCs mainly occurs from widely used consumer products: pharmaceuticals, personal care products, plastics and food preservatives, organochlorinated pesticides, phytoestrogens, hormonal agents, industrial solvents/

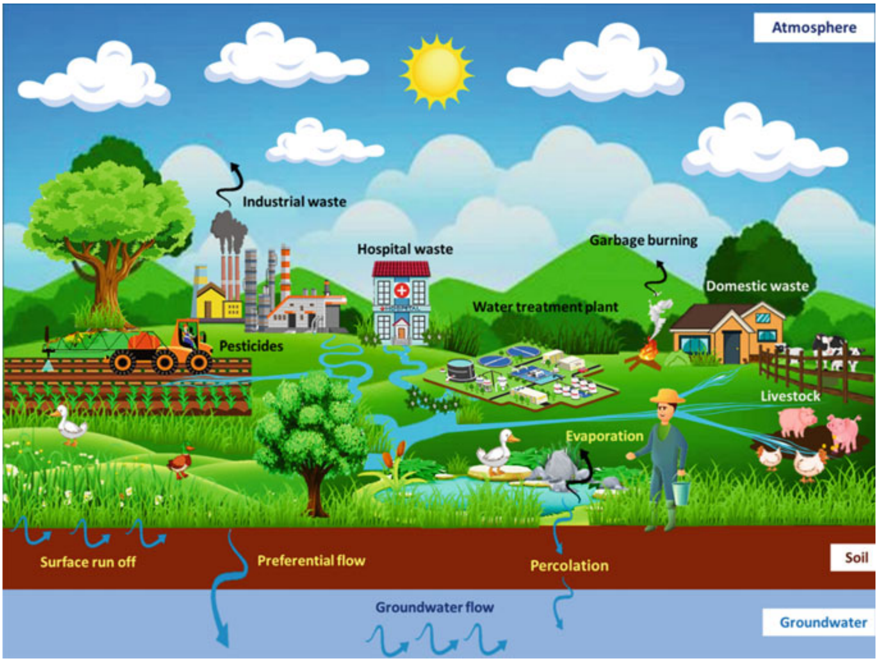

Fig. 6.1 Major sources of EDCs and their pathways in the environment

Table 6.1 Selected references showing the primary industrial and domestic sources of EDCs in the environment

Sources	EDCs	Reference
PPCPs (Pharmaceutical agents, detergents, soaps, cosmetics, toothpaste)	DES	Diamanti-Kandarakis et al. (2009)
	Iso-BP, *n*-BP	Mizuno et al. (2009)
	Triclosan	Cabana et al. (2007a), Soares et al. (2005)
	NP	Gao et al. (2020)
	DEP	Wang et al. (2018)
	4-*t*-OP	Rajendran et al. (2017a)
	Flutamide	Giesy et al. (2002), Sohoni and Sumpter (1998)
	Tamoxifen	Giesy et al. (2002), Sohoni and Sumpter (1998)
	Hydroxytamoxifen	Favoni and de Cupis (1998), Ramkumar and Adler (1995), Shelby et al. (1996)
	Nafoxidine, clomiphene	Favoni and de Cupis (1998), Sohoni and Sumpter (1998), Gaido et al. (1997)
	EE2	Stahlschmidt-Allner et al. (1997)
Plastics (industrial polymers)	BPA	Gao et al. (2020), Lee et al. (2005)
Plasticizers	Phthalates	Diamanti-Kandarakis et al. (2009)
	DBP	Lee et al. (2004)
	DEP	Wang et al. (2018)
	t-NP, 4-*t*-OP, 4-CP	Janicki et al. (2016), Legler et al. (1999), Soto et al. (1994)
Food (beer, sauces, soft drinks, jams, and pickles)	Parabens (alkyl hydroxy benzoates)	Routledge et al. (1998)
	Isobutylparaben (iso-BP) and *N*-butylparaben (*n*-BP)	Mizuno et al. (2009)
	t-Butylhydroxyanisol	Soto et al. (1995)
Lubricants, deformers, emulsifiers, paints, and surfactants	PCBs, PBBs, and dioxins	Beard et al. (1999), Diamanti-Kandarakis et al. (2009), Joyeux et al. (1997), Soto et al. (1995)
	NP	Cabana et al. (2007a), Soares et al. (2005)
	4-*t*-OP	Rajendran et al. (2017a), Soto et al. (1994)
	Butylphenol, pentylphenol	Nimrod and Benson (1997), Soto et al. (1995)
	Pentachlorophenol	Beard et al. (1999)

(continued)

Table 6.1 (continued)

Sources	EDCs	Reference
	Nonylphenol polyethoxylates	Priac et al. (2017), Servos (1999)
	Polyethoxycarboxylates	
Pesticides (fungicides, Insecticides, and herbicides)	Methoxychlor, chlorpyrifos, DDT, and vinclozolin	Diamanti-Kandarakis et al. (2009), Giesy et al. (2002)
	NP	Gao et al. (2020), Soares et al. (2005)
	Methoxychlor	Lee et al. (2006), Shelby et al. (1996)
	Diethyl phthalate	Soto et al. (1994)
	Atrazine, simazine	Legler et al. (1999), Petit et al. (1998), Soto et al. (1994)
	Endosulfan, dieldrin, lindane, toxaphene, methyl parathion, chlordecone, chlordane	Klotz et al. (1996)
	Carbamate insecticides (aldicarb, bendiocarb, carbaryl, methomyl, oxamyl)	Go et al. (1999)
	Pyrethroid insecticides (sumithrin, fenvalerate, d-tran, allethrin, permethrin)	
Domestic sewage (hormones excreted by humans, domestic or farm animals, wildlife) and municipal sewage	E2, EE2	Suzuki et al. (2003)
	E2, EE2, E1, E3	Svenson et al. (2003)
Trace metals	Cations of cadmium, cobalt, copper, mercury, nickel, zinc	Laskey and Phelps (1991)
	Lead	Ronis et al. (1998)
	Cadmium	Lafuente et al. (1997), Ricard et al. (1998)

Note: Bisphenol A; BPA, Iso-BP, isobutylparaben; *n*-BP, *n*-butylparaben; DES, diethylstilbestrol; DEP, diethyl phthalate; DBP, dibutyl phthalate; DDT, dichlorodiphenyltrichloroethane; PCBs, polychlorinated biphenyls; PBBs, polybrominated biphenyls; NP, nonylphenol; *t*-NP, *t*-nonylphenol; 4-*t*-OP, 4-*tert*-octylphenol; 4-CP, 4-cumylphenol; E1, estrone; E2, steroidal hormones 17β-estradiol; E3 estriol; EE2, 17α-ethinylestradiol; SWCNTs, single-wall carbon nanotubes; MWCNTs, multiwall carbon nanotubes

lubricants, and their by-products (González-Casanova et al. 2020; Kabir et al. 2015; Manikkam et al. 2013; Mottier et al. 2014).

Based on the legal aspects, EDCs can be categorized as regulated and nonregulated pollutants. Dioxins, polyaromatic hydrocarbons, polychlorinated biphenyls, and chlorinated organic pesticides belong to legal regulations. EDCs such as bisphenol A, steroid sex hormones, metal complexes, alkylphenol ethoxylates, derivatives of phthalates, personal care products (PCPs), brominated flame retardants (BFRs), nonionic surfactants, pharmaceuticals' residues, gasoline additives, and synthetic musk compounds which are not subjected to the legal regulations are referred as nonregulated EDCs (Kudłak et al. 2015). Bisphenol A (BPA), nonylphenols (NPs), and triclosan (TCS) have been identified as the most common EDCs due to their greater persistence in the environment (Gao et al. 2020).

Bisphenol A is used in epoxy resins, polycarbonate plastics, dental sealants, and various food and beverages packages. Due to the high global consumption of the plastic products, the presence of BPA in the environment is increasing (Huang et al. 2012). Although BPA is a hazardous chemical, people tend to use PBA-containing products such as food containers and canned foods (Hoepner et al. 2016). Nonylphenols and their ethoxylates are emerging EDCs used in industry as surfactants or raw materials for detergents (Gao et al. 2020).

Common household products, including detergents, PCPs, insecticides, lubricants, deformers, emulsifiers, and paints, can become sources for NPs and associated ethoxylates (Chokwe et al. 2017). When considering the pharmaceuticals and personal care products (PPCPs), diethylstilbestrol (DES) is a well-known pharmaceutical agent, and TCS is a broad-spectrum antibacterial agent and preservative which is widely used in personal care products (PCPs) which are identified as emerging EDCs (Ellis 2006; Saadi et al. 2019; WHO 2013). Natural estrogens (e.g., E1, E2, and EE2), estradiol, and estriol are also recognized as highly persisting ECDs in the environment (Ting and Praveena 2017). Methoxychlor, chlorpyrifos, dichlorodiphenyltrichloroethane (DDT), and vinclozolin are some of the main EDCs, which can enter the environment through pesticides and fungicides (Diamanti-Kandarakis et al. 2009; Giesy et al. 2002).

6.1.3 Effects of EDCs on the Living Beings When They Expose to EDCs

Living beings have an enhanced probability of being exposed to the various kinds of EDCs in different routes with the use of goods based on chemicals. Food, dust, air, soil, and water can be considered the main pathways for the transportation of EDCs. Ingestion, inhalation, and dermal contact are the identified routes of human and animal exposure to EDCs (Kudłak et al. 2015). Both the acute and chronic exposure of EDCs may influence the whole ecosystem while arising severe issues such as imbalanced ecosystem, change in the sexual characteristics of fishes, and increasing human health risk, decreased fertility, and cancer incidence (Aris et al. 2014). EDCs have a high ability to elicit harmful effects on male and female reproductive health, sex ratio, breast development, and metabolism rate. Further, EDCs can influence disorders in bone, adrenal and thyroid glands, hormone-related cancers, and the obesity of the body (Kudłak et al. 2015).

Human exposure to EDCs may affect sperm quality, fertility, and implantation resulting in premature delivery, abnormally developed infants, endometriosis, and cancer progression (Autrup et al. 2020; Sifakis et al. 2017). Sperm quality and steroidogenesis of mammals including rodents, dogs, cows, and goats and birds such as crows which are highly exposed to municipal or industrial sewage and dumping may also be affected (Nelson et al. 2019; Rhind 2005). They may cause altered female progeny, accelerated vaginal opening, estrous cycle disruption, pregnancy dysfunction, and uterine lesion (Fowler et al. 2012; Sifakis et al. 2017). Baby aquatic organisms are too sensitive to acute exposure of EDCs due to less tolerance in their early stages of life (Aris et al. 2014; Liu et al. 2011). EDCs also influence the usual eggs, fertility, and sperm quality of the fishes, frogs, and turtles (Campbell et al. 2006). Aquatic organisms exposed to EDCs may have increased mortality, sex ratio change, secondary sexual feminization, vitellogenin induction, and ovarian retraction (Campbell et al. 2006; You and Song 2021). The epidemiological, in vitro, and animal studies have proven that EDCs like phthalates, bisphenols, polyfluoroalkyl compounds, organotins, alkylphenols, organochlorines, dioxins, and brominated flame retardants can associate with obesity, insulin resistance, liver abnormalities, increased cholesterol levels, adipogenesis induction, metabolic syndrome, resistive expression, and diabetes (Kumar et al. 2020). Consequently, the acute exposure of EDCs may cause long-term known or unknown impacts to the whole ecosystem (Liu et al. 2008).

6.1.4 Fate and Transport of EDCs in the Environment

Three types of EDCs can be identified based on the environmental fate: persistency, mobility, and bioaccumulative pollutants (Kudłak et al. 2015). Persistency pollutants have a high ability to retain in the environment during the degradation process without being changed or transformed into other forms. Mobility pollutants maintain their movements with a vector within or between the transportation media. Bioaccumulative pollutants can accumulate or be stored in plant and animal tissues when organisms directly consume such pollutants containing food and water or are contacted indirectly to various environmental pollution sources. The pollutants can undergo biodegradation, elimination hydrolysis, photodegradation, sedimentation, accumulation, and sorption on the particulates suspended in water (Kudłak et al. 2015). As illustrated in Fig. 6.1, environmental contamination of EDCs can occur in different pathways such as through the surface and underground runoff, preferential flow, and infiltration of wastewater. When EDCs are released into the environment, there is a high tendency to mix them into the different environmental media like air, water, and soil. Many studies have reported that EDCs have been found in wastewater, surface water, sediment, drinking water, aquatic life, and even air (Braga et al. 2005; Campbell et al. 2006; Petrovic and Barcelo 2004; Shao et al. 2005). When EDCs containing sewage are released, primarily EDCs mix with the surface water or soil. Finally, they enter the surface water resources such as rivers, lakes, ponds, and waterfalls. The level of sorption may depend on the different chemical and physical

Fig. 6.2 Fate and the distribution of EDCs when they come to the aquatic environment. **Note:** *1*: Direct discharge of wastewater containing EDCs; *2*, *3*: bioaccumulation of EDCs to aquatic organisms and plants via water or food webs; *12*, *14*: ingestion of EDCs to domestic animals and soil organisms; *4*: sedimentation or accumulation of EDCs; *5*: percolation of EDCs; *6*, *7*: human exposure of EDCs; *8*: evaporation of EDCs; *9*: condensation of EDCs; *10*: precipitation of EDCs; *11*: adsorption of EDCs to the soil; *13*: EDCs intake from trees through absorption; *15*: transpiration-assisted transportation of EDCs

properties of the EDCs (Kudłak et al. 2015). The groundwater phase of the soil is then contaminated through infiltration or preferential flow, and finally, all water resources may be contaminated through the underground runoff of EDCs containing water. In addition, the direct exhaustion of EDCs containing fumes and air into the atmosphere leads to air contamination (Cincinelli et al. 2003). The overall fate and the distribution of EDCs can be illustrated conceptually as appears in Fig. 6.2.

According to Fig. 6.2, after discharging EDCs containing wastewater from sewage treatment plants to the water resources, especially to the ocean, the sorption process of EDCs primarily happens with water molecules or the organic materials in the water. Aquatic organisms such as fishes, invertebrates, and phytoplankton have to face a high risk when consuming EDCs uptaken by plants or when they are an intermediate of a food web (Aris et al. 2014; Aydin and Talinli 2013). Thus, the bioaccumulation of EDCs can occur inside their body through the ingestion and inhalation of EDCs. Further, the water-soluble EDCs or EDCs adsorbed or absorbed into the water-soluble organic materials have a high tendency to bioaccumulate in aquatic plants. Predicting the fate of EDCs is not simple, because EDCs in the water may also undergo the processes such as sedimentation or accumulation on the soil inside the water resource. Then the long-term dissolution of EDCs may happen from the accumulated and sediment EDCs when they mix with groundwater. As existing complex food webs in the environment, the distribution of EDCs is not limited to the ecosystem inside the water resource. Other organisms like eagles, seagulls, sea lions, tortoises, turtles, and penguins that depend on the aquatic organisms while circulating inside food webs are also affected by water-soluble EDCs. Domestic animals like dogs, cats, and municipal birds like crows are also at risk when they depend on seafood. Then the bioaccumulation of EDCs happens further. Massive human exposure of EDCs occurs via inhalation and ingestion. Through the fisheries, drinking water, green leaves, and all the other crops, there is an enormous probability to ingest EDCs into the human body. According to Figs. 6.1 and 6.2, it seems that EDCs are released to the environment not only directly from the industries and dumping burnings but also indirectly from water evaporation and plant transpiration. Therefore, all organisms are at risk during their respiration because they may inhale EDCs contaminated air.

As illustrated in both Figs. 6.1 and 6.2, the plants around the water resource, sewage system, or EDCs discharging sources may have a prohibitive chance to bioaccumulate while they are uptaking water. At the end of that plant process, EDCs may be released into the atmosphere through the transpiration process. The evaporation of contaminated water from EDCs and the correlation of EDCs with the wind facilitate EDCs distribution in the atmosphere (Annamalai and Namasivayam 2015). The condensation of EDCs containing vapor finally results in contaminated precipitation (Van Ry et al. 2000). Then the environmental contamination of EDCs befalls. Usually, sewage treatment plants are available in most countries to treat the sewage systems. Although the sewage is subjected to the cleaning process, when the treated aqueous phase or sludge phase is released, they may contain EDCs furthermore. The discharged aqueous phase contaminates both surface water and sediment, while the discharged sludge phase causes pollute soil, interstitial water, and groundwater. This contamination can be controlled by obliterating EDCs from the industrial, domestic, and municipal sewage during the sewage treatment process (Liu et al. 2008).

6.2 EDCs Degrading Microbes and Their Bioremediation Mechanisms

The primary pathways for the natural degradation of chemical contaminants in nature are facilitated by microorganisms (McNally et al. 2009). Hence, the microorganisms belonging to a diverse range of taxonomical groups such as fungi, bacteria, and algae can be used as biodegradation agents for different EDCs (Table 6.2). Microorganisms degrade complex chemical compounds into simple compounds with smaller molecular weight or end products such as CO_2 and H_2O as a part of their metabolic process (Shi et al. 2010). Therefore, the microorganism-driven degradation of chemical contaminants is directly influenced by the specific enzymes produced by them. Consequently, certain microbial strains are effective

Table 6.2 Selected reference on biodegradation of EDCs in terms of taxonomical groups, microorganisms, and targeted chemicals

Taxonomical group	Microorganism	Degraded EDCs	Reference
Fungi	*Stereum hirsutum* and *Heterobasidion insulare* (lignin-degrading basidiomycetes)	Bisphenol A	Lee et al. (2005)
	Coriolopsis polyzona (white-rot fungi)	Nonylphenol and bisphenol A and the personal care product ingredient triclosan	Cabana et al. (2007a)
	Trametes versicolor (white-rot fungi)	Isobutylparaben (iso-BP) and *n*-butylparaben (*n*-BP)	Mizuno et al. (2009)
	Phanerochaete chrysosporium, *Trametes versicolor*, and *Daldinia concentrica* (white-rot fungi)	Dibutyl phthalate	Lee et al. (2004)
	Phanerochaete chrysosporium, *Pleurotus ostreatus*, *Trametes versicolor* and *Bjerkandera* sp. BOL13 (white-rot fungi)	Nonylphenol	Soares et al. (2006), Soares et al. (2005)
	Pleurotus ostreatus (while rot fungi)	di-(2-ethylhexyl)phthalate	Ahuactzin-Pérez et al. (2018)
	Agromyces sp. MT-O strain	di-(2-ethylhexyl)phthalate	Zhao et al. (2016)
	Irpex lacteus 617/93, *Bjerkandera adusta* 606/93, *Phanerochaete chrysosporium* ME 446, *Phanerochaete magnoliae* CCBAS 134/I, *Pleurotus ostreatus* 3004 CCBAS 278, *Trametes versicolor* 167/93, *Pycnoporus cinnabarinus* CCBAS 595, *Dichomitus squalens* CCBAS 750 (ligninolytic fungal strains)	4-*n*-nonylphenol, technical 4-nonylphenol, bisphenol A, 17α-ethinylestradiol, and triclosan	Cajthaml et al. (2009)
	Trametes pubescens MUT 2400 (white-rot fungi)	Salicylic acid, naproxen, diclofenac, ketoprofen (anti-inflammatory drugs), and estrone and ethinylestradiol (hormones)	Spina et al. (2013)
	Umbelopsis isabellina (non-ligninolytic fungus)	Nonylphenol, 4-*tert*-octylphenol, and 4-cumylphenol (*t*-NP, 4-*t*-OP, 4-CP)	Janicki et al. (2016)

(continued)

Table 6.2 (continued)

Taxonomical group	Microorganism	Degraded EDCs	Reference
	Saccharomyces cerevisiae (yeast)	Municipal sewage	Svenson et al. (2003)
		Estradiol (E2)	
		Ethinylestradiol (EE2)	
		Estrone (E1)	
		Estriol (E3)	
	Candida rugopelliculosa (yeast)	Alkylphenols	Rajendran et al. (2017a)
	Stereum hirsutum	Shown high resistance to methoxychlor (MXC)	Lee et al. (2006)
	Fusarium falciforme RRK20	4-*t*-Octylphenol (4-*t*-OP)	Rajendran et al. (2017b)
Bacteria	Novel endophytic strain YJB3 *Bacillus megaterium*	Dibutyl phthalate	Feng et al. (2018)
	Rhizosphere bacteria TIK1 and IT4	Nonylphenol and Triclosan	Ramírez-Cavazos et al. (2014), Toyama et al. (2013)
	Purified LacI and LacII isoforms produced by *Pycnoporus sanguineus*	Phenolic EDCs	
Algae	Freshwater microalgae, *Chlamydomonas mexicana*, and *Chlorella vulgaris*	Bisphenol A	Ji et al. (2014)
	Microalgae, *Selenastrum capricornutum*, and *Chlamydomonas reinhardtii*	Estradiol (E2), Ethinylestradiol (EE2)	Hom-Diaz et al. (2015)
	Marine microalga *Amphidinium crissum*	Bisphenol A	Shimoda et al. (2011b)
	Marine microalga *Chrysocampanulla spinifera* and *Amphidinium crassum*	Benzophenone	Shimoda et al. (2011a)

only against the degradation of the specific EDCs. Endocrine-disrupting activity is linked mainly with natural and synthetic hormones estrone (E1), 17β-estradiol (E2), estradiol (E3), and 17α-ethinylestradiol (EE2), xenoestrogens bisphenol A (BPA) and nonylphenol (NP), and manufactured chemicals such as PPCPs. Some microorganisms such as bacteria, microalgae, and fungi enormously support the biodegradation of EDCs, making them less endocrine-disrupting active or less harmful (Lee et al. 2006; Soares et al. 2005).

6.2.1 Degradation of EDCs by Bacteria

Bacteria are heterotrophic prokaryotic organisms and showed high efficiencies for the degradation of EDCs by adsorption, accumulation inside cell compartments, and degradation through enzymatic mechanisms as shown in Fig. 6.3 (Roccuzzo et al.

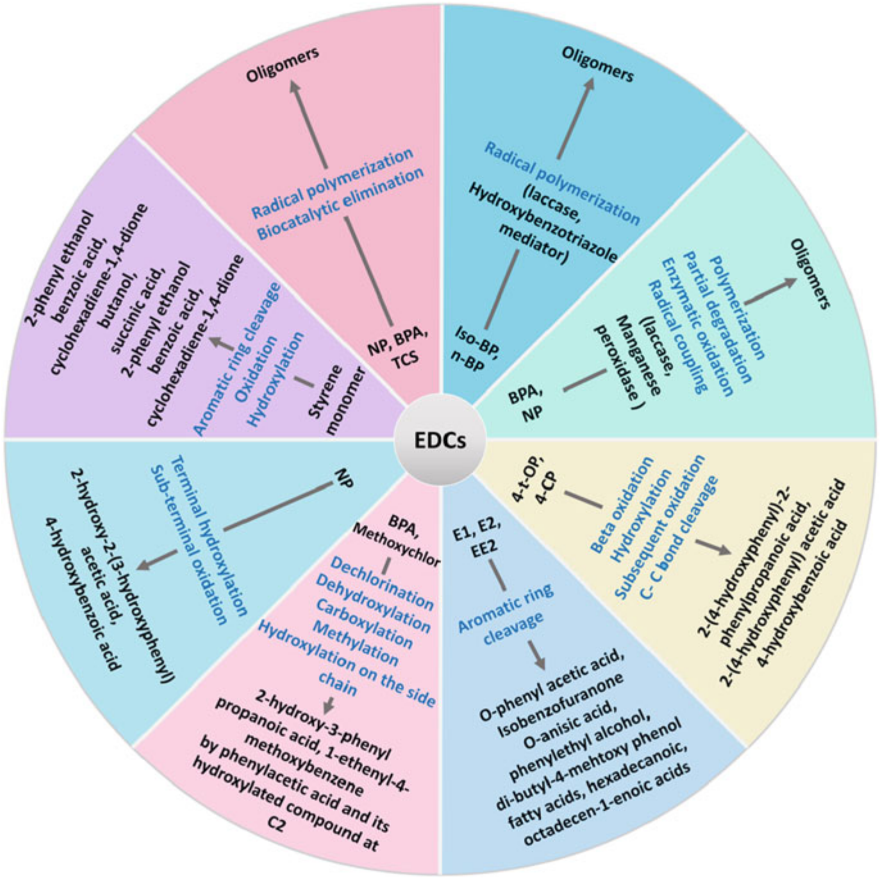

Fig. 6.3 Possible mechanisms and their products for the degradation of different types of EDCs in the presence of microorganisms and their corresponding enzymes

2020; Yu et al. 2013). They produce several enzymes, including hydrogenase, dehydrogenase, dioxygenase, hydroxylase, transferase, and laccase, demonstrating high efficiencies toward the biodegradation and biotransformation of a wide range of EDCs (Wojcieszyńska et al. 2020). Furthermore, extensive studies have been conducted toward the bioremediation of hormonal EDCs via bacterial degradation. Bacteria can degrade steroidal hormones via two degradation pathways, namely, metabolic (growth-linked) and co-metabolic (non-growth-linked) (Yu et al. 2007). During metabolic pathways, bacteria utilize hormones as a carbon source for energy production, while co-metabolic pathways do not provide any carbon or energy source (Yu et al. 2013).

Novosphingobium tardaugens (strain ARI-1) is considered as the E2-degrading bacterium firstly identified from activated sludge (Fujii et al. 2002). *Rhodococcus equi and Rhodococcus zopfii* (Yoshimoto et al. 2004), *Achromobacter xylosoxidans* and *Ralstonia pickettii* (Weber et al. 2005), *Sphingomonas* sp. and *Aminobacter* sp. (Yu et al. 2007), *Bacillus* sp. (Jiang et al. 2010), and *Brevundimonas diminuta* (Muller et al. 2010) strains were very effective for the E1 and E2 degradation. The main mechanism of E2 degradation was transformation into E1. Yu et al. (2007) have studied 14 isolates that were capable of transformation of E2 to E1, and only three strains (strains KC6–8) out of 14 were able to degrade E1. Moreover, *Novosphingobium tardaugens* (strain ARI-1) can degrade E1 and E3 effectively. A recent study on estrogen degraders in an activated sludge further confirmed that *Novosphingobium* spp. is as a major estrogen degrader (Chen et al. 2018). Mainly E2 conversion into E1 reactions is associated with dehydrogenation reactions with the involvement of bacterial 17β-hydroxysteroid dehydrogenase enzymes responsible for the 17-dehydrogenation of E2 (Chen et al. 2017).

Few other species have been identified as E2 degradation bacterium into E1. However, further metabolism of E1 was not reported yet. Ke et al. reported that bacteria, LHJ1 and LHJ3, belong to the genus *Acinetobacter* and *Agromyces* and oxidize E2 to E1 under aerobic conditions (Ke et al. 2007). In addition to *Aminobacter* sp., Yu et al. (2007) showed that different genera *Brevundimonas* (strain KC12), *Escherichia* (strain KC13), *Flavobacterium* (strain KC1), *Microbacterium* (strain KC5), *Nocardioides* (strain KC3), *Rhodococcus* (strain KC4), and *Sphingomonas* (strains KC11 and KC14) could transform E2 to E1 within 7 days. The degradation pathways of E2 by aerobic bacteria mainly start with 17-dehydrogenation of D-ring at the C17 position. Then it is further degraded by hydroxylation of aromatic ring at the C4 position. Finally, pyridinestrone acid was detected as a metabolite that exhibits negligible estrogenic activity.

Many studies have reported BPA degradation ability of *Pseudomonas* sp. under aerobic conditions. Among those, *Pseudomonas putida* strains were very effective microorganisms for the biodegradation of BPA found in the river water (Kang and Kondo 2002) under aerobic conditions. Degradation of BPA was hardly found under anaerobic conditions. Moreover, *Pseudomonas putida* strain was identified with nonylphenol polyethoxylates degradation ability (John and White 1998; Tanghe et al. 1999). Lobos et al. reported a novel gram-negative, aerobic bacterium (strain MV1) as a BPA degradation bacteria, thereby revealing major and minor pathways of bisphenol A biodegradation (Lobos et al. 1992). *Rhodococcus* sp. L4 degraded a mixture of PAE compounds including DMP, DEP, and DBP (Lu et al. 2009). Surhio et al. (2014) observed 99% degradation of DMP by bacterial strain, *Bacillus thuringiensis*. Thus, Surhio et al. (2017) specified, 82–96% biodegradation of PAE mixture comprising DMP, DEP, DPP, and DBP using *Bacillus thuringiensis*. In addition, the aerobic degradation of styrene by *Rhodococcus* gram-positive bacteria species has been described emphasizing its degradation pathways as initial oxidation of the vinyl side chain and the direct attack at the aromatic nucleus (ring cleavage) (Grbić-Galić et al. 1990; Warhurst et al. 1994). Dehydrogenase facilitates the oxidation of the side chain, while the aromatic ring cleavage undergoes through the 3-vinylcatechol production.

6.2.2 Fungal Degradation of EDCs

Fungi, compared to bacteria, showed high tolerance for a wide range of pollutant concentrations as they are more robust in the environment (Ellouze and Sayadi 2016). Therefore, fungi are the most widely used microorganism taxa for the degradation of a wide variety of EDCs (Table 6.2). Among them, different strains of white-rot fungi, a group of litter-decomposing fungi that mostly comprises basidiomycetes, showed extremely high performance to remediate a range of organic EDC compounds in the presence of various kinds of enzymes extracted from them (Asgher et al. 2008). They have a high ability to initiate lignin degradation in the presence of nonspecific extracellular enzymes, such as lignin peroxidase, manganese-dependent peroxidase, manganese-independent peroxidase, cytochrome p-450, and laccase. The nonspecificity of these enzymes allows degrading the aromatic xenobiotics, such as pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, dyes, polymers, and wood preservatives (Pointing 2001). H_2O_2-forming glyoxal oxidase, aryl alcohol oxidase, oxalate producing oxalate decarboxylase (ODC), NAD-dependent formate dehydrogenase (FDH), and P450 monooxygenase like accessory enzymes have also been extracted from different kinds of WRF strains (Wesenberg et al. 2003).

Laccase from fungi is a multi-copper oxidase that acts as the catalyzer for the single electron oxidation of phenolic compounds by taking place the reduction of molecular oxygen to water (Lontie 1984). The laccase has shown extremely promising results for the degradation of various xenobiotics, including EDCs (Cabana et al. 2007b; Lloret et al. 2012). Laccases are oxidoreductase enzymes, and their low substrate specificity enables them to degrade a wide range of EDCs. These enzymes can directly act on substrates bearing low redox potential such as phenols and oxidize them (Bourbonnais et al. 1998; Tadesse et al. 2008). As well, with the help of diffusible electron carriers (laccase redox mediator compounds) laccases are able to oxidize large compounds with high redox potential (Call and Mücke 1997; Mäkelä et al. 2020). However, applying whole fungal cells for bioremediation generates severe problems in sustainable operation and economic aspects. Therefore, the extracellular application of laccases extracted from fungal cultures is considered an eco-friendly approach with easy process control and low energy use (Spina et al. 2013). Becker et al. (2017) found that the extracellular application of laccases, even at very low concentrations such as 2.8 of 2,2′-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) units/L, is highly efficient for the hormonal EDCs degradation. Other than laccases, fungi-produced manganese peroxidase and lignin peroxidase degrade many xenobiotic species, including EDCs in the environment (Ellouze and Sayadi 2016). In the presence of hydrogen peroxide, MnP catalyzes Mn(II) to Mn(III) oxidation. The generated Mn(III) chelation and release from the manganese-binding sites of MnP is supported by the malonate, oxalate, and α-hydroxy acids, such as malate, lactate, and tartrate. The formed Mn (III)-organic acid complexes are then oxidized forming different phenolic compounds (Glenn et al. 1986; Warhurst et al. 1994).

From the enzyme preparation of *Coriolopsis polyzona* WHF, the biocatalytic elimination of NP, BPA, and TCS has been studied, and the mechanism behind the bioremediation is reported as radical polymerization. The by-products are different oligomers produced through C–C or C–O bond formations (Cabana et al. 2007a). Isobutylparaben (iso-BP) and *n*-butylparaben (*n*-BP) are also degraded in the presence of both laccases from the white-rot fungus *Trametes versicolor* and 1-hydroxybenzotriazole (HBT) mediator, where there is a capability of laccase to degrade the pollutant alone. BPs are oxidized by the free radicals generated from laccase and HBT reactions (Mizuno et al. 2009). BPA and NP were also degraded by using manganese peroxidase (MnP) and laccase extracted from WRF with the aid of HBT. The mechanism behind it has been reported as polymerization and partial degradation followed by enzymatic oxidation (Call 1994). Thus, it is revealed that the enzymatic treatment of BPA and NP resulted in oligomers through the phenoxy radical formation followed by the radical coupling mechanism (Tsutsumi et al. 2001).

Laccase and MnP from the *Phanerochaete chrysosporium* ME-446 and *Trametes versicolor* IFO-6482 WRF with HBT as the mediator were used to degrade the steroidal hormones E2 and EE2 followed by cleaving the aromatic ring (Suzuki et al. 2003). However, the mechanism, the roles of the intermediates, and the metabolites are not well defined. Lee et al. (2004) have reported that *O*-phenyl acetic acid, isobenzofuranone, *O*-anisic acid, phenylethyl alcohol, dibutyl-4-mehtoxy phenol, and fatty acids such as tetradecanoic, hexadecanoic, and octadecen-1-enoic acids are identified as the intermediates of the degradation mechanism. Moreover, it has been reported that the most abundant biodegradation products of BPA and methoxychlor from the two lignin-degrading basidiomycetes, *Stereum hirsutum* and *Heterobasidion insulare*, are identified as 2-hydroxy-3-phenylpropanoic acid, followed by 1-ethenyl-4-methoxybenzene and then by phenylacetic acid and its hydroxylated compound at C2. In this study, it is assumed that the origination of these products is from the phenyl part of the BPA. Thus, degradation is basically through dechlorination, dehydroxylation, carboxylation, methylation, and hydroxylation on the side chain (Lee et al. 2005). Another study has also studied the degradation of BPA from MnP from *P. ostreatus* WRF, and the predominant major metabolites were recognized as phenol, 4-isophenyl phenol, 4-isopropyl phenol, and hexestrol. From these two studies, it can be concluded that the degradation of BPA is along with the formation of different kinds of phenolic metabolites.

According to Lee et al. (2006), the estrogenic effects of styrene monomer, considered as a suspected EDC, can be reduced by *Phanerochaete chrysosporium* KFRI 20742, *Trametes versicolor* KFRI 20251, and *Daldinia concentrica* KFRI 40-1 strains. 2-phenyl ethanol, benzoic acid, cyclohexadiene-1,4-dione, butanol, and succinic acid are the major metabolites of this degradation mechanism. Some minor metabolites produced via oxidation and hydroxylation of styrene monomer are 2-phenyl ethanol, benzoic acid, and cyclohexadiene-1,4-dione. Aromatic ring cleavage is also addressed there, and the by-products of that mechanism are butanol and succinic acid. Tamagawa et al. (2005) treated endocrine-disrupting genistein with *Phanerochaete sordida* YK-624 WRF under the ligninolytic condition with low-nitrogen and high-carbon culture medium and the underlying mechanism was interpreted as the polymerization followed by the enzymatic oxidation at the para-substituted phenyl moiety (Tamagawa et al. 2005). In the study Janicki et al. (2016), the metabolizing capability of *Umbelopsis isabellina* (Zygomycota) fungus to degrade NP, 4-*tert*-octylphenol (4-*t*-OP), and 4-cumylphenol (4-CP) has been studied (Janicki et al. 2016). The reaction mechanism of 4-*t*-OP has been shown as the beta-oxidation in the enzyme-rich medium. 2-(4-hydroxyphenyl)-2-phenylpropanoic acid, 2-(4-hydroxyphenyl) acetic acid, and 4-hydroxybenzoic acid were recognized as key metabolites of the microbial decomposition of 4-CP. This study revealed that the decomposition was initiated at the carbon atom of the C-8 or C-9 methyl groups by the hydroxylation and the subsequent oxidation of the corresponding carboxyl group. Additionally, several rearrangements and C–C bond cleavage also can happen during the decomposition. Shortening the alkyl moiety and detachment of methyl groups from the alpha carbon were identified as starting activities in the 4-*t*-OP degradation mechanism. 2-hydroxy-2-(3-hydroxyphenyl)acetic acid and 4-hydroxybenzoic acid were detected as the intermediates of the NP degradation pathway, followed through the terminal hydroxylation and the sub-terminal oxidation processes (Janicki et al. 2016). Accordingly, the mechanisms, intermediates, and metabolites behind the EDCs degradation by fungi depend on the type of both fungi and EDCs.

6.2.3 Degradation of EDCs by Microalgae

The utilization of microalgae is considered an environmentally friendly and economically feasible method for the removal of EDCs from wastewater sources due to their marginal growth requirements, prevalent occurrence, and wide range of degradation mechanisms for pollutants (Singh et al. 2019). Microalgae can accumulate pollutants intercellularly and degrade them in an efficient manner (Newsted 2004; Yang et al. 2002). They possess the ability to degrade exogenous substrates using different enzymatic routes such as hydrolysis, hydroxylation, oxidoreduction, hydrogenation, and glycosylation. However, the glycosylation process showed high efficiencies on the bioremediation of EDCs such as bisphenol A by converting to the corresponding glycosides (Morohoshi et al. 2003).

Several other studies reported using microalgae such as *Chlamydomonas mexicana*, *Chlorella vulgaris*, and *Chlorella fusca* for successfully degrading BPA from aqueous systems (Hirooka et al. 2005; Ji et al. 2014). Hom-Diaz et al. (2015) have showed an effective removal of endocrine-disrupting hormones such as β-estradiol and 17α-ethynylestradiol from wastewater using microalgal species, *Selenastrum capricornutum* and *Chlamydomonas reinhardtii*. BPA was metabolized to BPA glycosides by four different microalgae *Pseudokirchneriella subcapitata*, *Scenedesmus acutus*, *Scenedesmus quadricauda*, and *Coelastrum reticulatum* (Nakajima et al. 2007). A similar study has shown the ability of various plant species (family Fabaceae and Brassicaceae) for the conversion of BPA to β-glucosides and suggested the involvement of BPA-specific glucosyltransferase (Nakajima et al. 2005). Estrogenic activity of BPA was decreased after biodegradation by algal (*Chlorella vulgaris*) and bacterial (*Aeromonas hydrophila*) in the aquatic environment (Gulnaz and Dincer 2009). Furthermore, studies demonstrated the use of immobilized microalgae cells for improved reduction and glycosylation of exogenous organic compounds including EDCs (Shimoda and Hamada 2009; Shimoda et al. 2011a). Additionally, microalgae produce oxygen through the photosynthesis process and provide to the heterotrophic bacteria, accelerating their organic contaminant-degrading abilities (Yan et al. 1995).

6.2.4 Bioremediation of Metallic EDCs from Microorganisms

Conversely, the metallic pollutants that act as EDCs cannot be degraded by microorganisms. However, microorganisms can reduce the bioavailability of metallic EDCs in the environment in several ways such as oxidation-reduction, transformation, binding, immobilization, and volatilization (Verma and Kuila 2019). However, the use of microbial-assisted design approaches to observe and regulate the growth and activity of microorganisms ensures the successful bioremediation of metallic pollutants. Bioleaching, bioaccumulation, biotransformation, biomineralization, and biosorption are mechanisms that utilize the bioremediation of metals (Verma and Kuila 2019). Table 6.3 shows the utilized microbial strains for bioremediation of heavy metals considered as EDCs.

Table 6.3 Selected studies showing the utilization of microorganisms for bioremediation of metallic EDCs

Taxonomical group	Microorganism	Metallic EDC/s	Reference
Fungi	*Aspergillus niger*	Cd, Zn	Rajendran et al. (2003)
	Rhizopus arrhizus	Cd	Favero et al. (1991)
	Pleurotus ostreatus	Cd, Cu, Zn	Rajendran et al. (2003)
	Ganoderma applanatum	Cu, Pb, Hg	Gabriel et al. (1996), Gabriel et al. (1994)
	Stereum hirsutum	Cd, Co, Cu, Ni	Gabriel et al. (1996), Gabriel et al. (1994)
	Bacillus sp.	Cu, Zn	Rajendran et al. (2003)
Bacteria	*Citrobacter* sp.	Cd, Pb, Co, Pb, Ni, Hg	Rajendran et al. (2003)
	Zoogloea sp.	Cu, Ni, Cd, Co, Ni	Sar and D'Souza (2001), Verma and Kuila (2019)
	Citrobacter sp.	Cu, Ni, Cd, Co, Ni	Sar and D'Souza (2001), Verma and Kuila (2019)
	Pseudomonas sp.	Hg	Giovanella et al. (2017)
	B50D		
	Paenibacillus sp.	Cu	Govarthanan et al. (2016)
Algae	*Phormidium valderium*	Cd, Pb, Cu, Ni, Co	Gabriel et al. (1996), Gabriel et al. (1994), Satyanarayana et al. (2012)
	Chlorella vulgaris	Cd, Pb, Co, Pb, Ni, Hg	Rajendran et al. (2003)

This description remarkably expands the understanding of microorganisms' degradation of EDCs, and bioremediation has proven to be a cost-effective mitigation strategy.

6.3 Future Directions

Bioremediation of EDCs by microbes provides several advantages, including low initial cost, long period removal process, and an easy and straightforward requirement for equipment and space, providing economically adequate environmental protection. However, application is yet to be developed for the real scale use. Therefore, more focused research should be driven toward improvements, optimization, and real application.

- The documented or currently practiced microbe-assisted EDCs treatment methods are required to optimize through proper method validation.
- Further studies are required to clarify and recognize the detailed pathway of microbial degradation mechanisms, metabolites, intermediates, possible degradation products, the structures of the resultants, and their estrogenic activity to enhance the risk related to the degradation process.
- The function of enzymes released by microbes during the degradation process should be elucidated to understand EDCs biodegradation.
- Investigations are needed to examine factors such as additional enzymatic substrates and supplementary nutrients that can positively influence and further enhance the efficiency of EDCs treatment process.
- The processes involved with lignin enzymes such as mechanism, isolation, immobilization, and characterization should be studied to explore the understanding of enzymatic hyperactivation and thermostabilization during EDCs degradation.
- Although many kinds of research have been performed as laboratory-level studies under model conditions, there is less documentation on the real-time field application. Consequently, in order to ensure the capability and applicability of microbial degradation of EDCs under natural environmental conditions, it is needed to apply the developed methods for industrial wastewater treatment.
- EDCs in actual wastewater can be reacted with different pollutants, thereby forming a cocktail of contaminants. Applying the already established microbial methods to actual wastewater may help understand the critical effects of other environmental pollutants.
- Instead of focusing only on one type of EDC and microbe as described in most research found in the current studies, it is necessary to find and study a microbe or a group of microbes that can degrade a wide range of EDCs in real-time wastewater. Then, the effects from the combined degradation could be identified intensively.

- To develop novel and ecologically sound bioremediation methods, especially the spatiotemporal stability of the association of two different microbes (e.g., bacteria–fungi associations) should be further studied.
- To reduce the hindrances in the microbial remediation process, the methodologies and ecological approaches that can sustain sufficient microbe biomass, enzyme production, and activity must be investigated.
- Several studies have confirmed that some fluctuations of EDCs such as BPA can vary the carbohydrate content in the algal cell membrane during the degradation process and influence the metabolic processes. Therefore, it may be beneficial to develop both bioremediation of EDCs and the generation of biofuel feedstock as a simultaneous dual strategy (Ji et al. 2014).

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Biological Treatment of Pharmaceuticals and Personal Care Products (PPCPs)

7

Sudipa Bhadra and Surajbhan Sevda

Abstract

In the global era, the use of pharmaceuticals and personal care products (PPCPs) has increased rapidly worldwide. In general, the PPCPs after being utilized/consumed are emitted into the sewage system and thereby into municipal waste material. With improper treatment of these wastes through conventional wastewater treatment, PPCPs easily seep into nearby soil and water and in turn contaminate our ecosystem. With regular addition of these compounds, there has been a significant increase in the amount of PPCPs material in the environment rendering them hazardous for aquatic as well as terrestrial animals and humans. Studies have also shown that PPCP compounds have percolated even into groundwater. Therefore, a proper mechanism is required for the removal of these PPCPs from drinking water, sewage, and environment. This chapter discusses conventional methods such as nanofiltration, reverse osmosis, and ozone with advanced oxidation along with focusing on mechanism and future perspective of the biological treatments that can be used for removal of PPCPs from contaminated sites.

Keywords

Pharmaceuticals and personal care products · Biological treatment · Wastewater · Physicochemical techniques

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7.1 Introduction

Pharmaceuticals and personal care products (PPCPs) are classified as chemically active ingredients also known as “emerging contaminants (ECs),” while pharmaceuticals are products that are majorly used in treating or preventing diseases and can be categorized into antibiotics, analgesics, blood lipid regulators, natural and synthetic hormones, β-blockers, antidiabetics, antihypertensive, non-steroidal anti-inflammatory drugs (NSAIDS), and many more (Liu and Wong 2013; Daughton and Ternes 1999; Yang et al. 2017). Products used every day for uplifting standard of living of humans such as cosmetics, shampoos and conditioners, soaps and detergents, and various other household products come under (PPCPs) (Ebele et al. 2017). Occurrence of these ECs in the environment has become a major concern because of their physiochemical properties and metabolically active compounds present in pharmaceuticals; they tend to have a hydrophobic nature, which easily enables them to bioaccumulate in the environment.

There are many ways by which PPCPs can enter into the environment. Discharge of waste materials from industries, hospitals, households, and wastewater treatment plants straight into surface water makes them contaminated with PPCPs. And leaching of these PPCPs into the groundwater makes them also contaminated. These PPCPs then finally enter into the food chain via irrigation and agricultural practices (Sui et al. 2015).

Conventional wastewater treatment plants are not effective in removing these ECs, and hence they persist in the environment.

Various studies have shown that PPCPs persist in our environment much longer than previously thought ranging from few months to even many years (Kumar et al. 2010; Monteiro and Boxall 2009). Because of their polar nature, PPCPs persist in surface water and then percolate to ground level during groundwater recharge, and in this process, few PPCPs do get removed, but compounds such as carbamazepine can easily percolate and reach groundwater with a travel time of up to 8 years (Chen et al. 2016a, b). To minimize the effects of these contaminants on the environment, the scientific community has raised questions about the presence, outcome, and consequences these PPCPs pose on our environment.

7.2 Issues Related to the Presence of PPCPs in Wastewater Streams

PPCPs when get release into the environment due to their physiochemical properties become persistent and start getting bioaccumulated. Individual PPCPs may not become persistence, but because these PPCPs get continuously deposited in the environment, they become “pseudo-persistent.” These pseudo-persistent compounds have much more persistence capability in the environment than the original pharmaceutical compounds since their source of origin continuously gets refilled although these compounds repeatedly get biodegraded and photodegraded by the environment (Houtman et al. 2004; Kar et al. 2020).

Because of the biologically active compounds present in PPCPs, when these chemicals are released into freshwater, they become harmful to many aquatic animals, even when present in very low concentration. The majority of these PPCPs being manufactured for humans and animals have a severe impact on non-target aquatic animals (Chen et al. 2016a, b).

Recent studies have shown that PPCPs have hazardous effects on fishes, they being the non-target organism. For example, a study showed that when gemfibrozil was exposed to goldfish (*Carassius auratus*) for 14 days, it got bioaccumulated in its plasma at a concentration factor of 113 (Mimeault et al. 2005). Another experiment conducted by Vernouillet et al. (2010) showed that carbamazepine (CBZ) which is an antiepileptic drug gets bioaccumulated by algae *Pseudokirchneriella subcapitata* at a bioaccumulation factor of 2.2, whereas the same compound gets bioaccumulated in crustacean *Thamnocephalus platyurus* at a concentration factor of 12.6. Yet another concerning factor that comes to light with PPCPs being accumulated in the environment due to overuse of these ECs in human medicine and animal husbandry is the generation of antibiotic-resistant strains inside a pool of natural population of bacteria, and this in turn has led to ineffective treatment of certain diseases that are caused by antibiotic-resistant bacteria (World Health Organization 2015).

One of the significant threats posed by PPCPs being present in water bodies is their potential to hinder the pathways of endocrine systems thereby producing undesirable effects or disturbance in homeostasis. Endocrine disrupters (ED) are compounds of exogenous nature that have the potential to change the working ability of the endocrine system and thereby affect the health of an organism and its progeny adversely (Wielogórska et al. 2015). Toxicity of certain PPCP compounds increases when they act synergistically, which implies that while singly these PPCPs may be present in low concentrations and not imply much toxic effects, when a cocktail of PPCP compounds work together, they impose significant toxic effects leading to severe ecotoxicity. This was shown by a study conducted by Cleuvers (2003) where carbamazepine and clofibric acid—two different drugs belonging to two different therapeutic classes—elicited more severe effects on *Daphnia magna* than when acting singly on the organism at the same concentration (Thorpe et al. 2001).

Studies of recent times have depicted that the toxicity due to exposure to PPCPs depends on the organism that has been exposed to it, the time duration to which it has been exposed, and the developmental stage at which it was exposed and at what concentration. More abnormalities are observed at crucial stages of development in non-targeted organisms even when PPCPs are present in trace amount (Wilkinson et al. 2016).

7.3 Existing Physicochemical Techniques

As already mentioned earlier, PPCPs are present in nature in very small amount, but the concern as well as the necessity to remove these compounds arises due to the reason that these are being introduced in the nature continuously. Methods to remove

PPCPs are broadly divided into physiochemical methods and biological methods. In this section we will focus on physiochemical methods.

7.3.1 Physical Adsorption Processes to Remove PPCPs

7.3.1.1 Adsorption

Adsorption is one of the most commonly used physical techniques to remove organic PPCP compounds from the environment especially from polluted water. Various research has been done to increase the removing efficiency of PPCPs from aqueous environment using discrete adsorbents. The below section focuses only on the carbon-containing materials used for adsorption of PPCPs because they are cheap, are easily available, and are also effective in removing PPCPs.

Activated Carbon

Activated carbon has long been used in the treatment of water, and its performance in removal of endocrine disruptors has been reported by Liu et al. (2009). The result of the study was positive; however, over time, two problems occurred. First, the adsorption capacity decreased and, second, the quality of the activated carbon got deteriorated. The main types of activated carbon are powdered activated carbon (PAC) and granular activated carbon (GAC), and the efficiency of these activated carbons to capture PPCPs depends on the hydrophobicity and charge of the PPCPs. Apart from these, even the water matrix has an effect on the adsorption capability of the activated carbon (Mailler et al. 2015; Rodriguez et al. 2016).

Graphene and Graphene Oxide

Recent studies have shown that both graphene and its oxide can be used to extract PPCPs, and their efficiency to remove them depends on physiochemical properties of PPCPs. Apart from this, the pH and the time of contact also influence the efficiency rate of PPCPs removal (Kyzas et al. 2015; Yang and Tang 2016). Because graphene and its oxide comparatively have more surface area than activated carbon, they have become one of the preferred adsorbents to remove PPCPs. More research needs to be carried out on graphene and graphene oxide, to study real wastewater and its effect on the adsorption capacity of PPCPs by these compounds.

Carbon Nanotubes

Carbon nanotubes (CNTs) are composed of graphene sheets, and they can be arranged as single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) (Czech and Buda 2016). Because CNTs have an extraordinary capacity of sorption, they also have a very high specific surface area-to-mass ratio which ranges between 75 and 1020 m^2/g (Jung et al. 2015). CNTs form three types of chemical bonds—hydrophobic interactions, van der Waals forces, and π-π stacking—which allow them to create four distinct sites of adsorption such as inner cavities, interstitial channels, external grooves, and outermost surfaces (Ye et al. 2019; Wei et al. 2013).

$BiVO_4$ is a semiconductor which is used for degrading pollutants of organic nature. In a study using MWCNT/$BiVO_4$ composites, photocatalytic degradation of oxytetracyclines using high-performance liquid chromatography (HPLC) was measured, and the value reached 88.7% in a duration of 60 min. Because of the synergistic effect that happened between MWCNT and $BiVO_4$ composites, such an enhanced rate of photocatalytic degradation was achieved (Marques et al. 2013).

7.3.1.2 Coagulative Precipitation

Coagulative precipitation is one of the first methods that are applied to remove PPCPs. It works on the principle of colloidal coalescence, bonding, and precipitation due to gravity (Yuan et al. 2016). Coagulants help in the process of adsorption and flocculation of the wastewater and also increase the biodegradability of organic and inorganic wastes. Coagulants that are frequently used are broadly categorized into two main groups: (1) coagulants made up of inorganic salts such as aluminum and iron salts and (2) coagulants made up of polymers, both organic such as polyacrylamide and inorganic such as polyaluminum chloride (PAC) and polyferric sulfate (PFS). However, there are few disadvantages of this method such as slow removal rate of dissolved wastes, production of huge amount of chemical sludge, and incomplete treatment of pathogens.

7.3.1.3 Flotation

Flotation can be applied to both solid-liquid and liquid-liquid interface and is an easy method which is applied to remove micropollutant particles. Processes such as electroflotation, induced air flotation, and dissolved air flotation allow these micropollutant particles to have a density lower than that of the water, thereby allowing these micropollutants to rise and float on the surface of water and henceforth be removed (Suarez et al. 2009). This method being simple has an added advantage of being economical, consumes less power, and is easy to maintain.

7.3.1.4 Membrane Separation

Membrane separation is an adequate traditional process which uses membranes of varying sizes and materials for diffusion dialysis, electrodialysis, reverse osmosis, and ultrafiltration (Martínez et al. 2013). This process is cheap and easy to handle with low production of sewage output making them convenient for primary treatment of wastewater. But there are a few disadvantages also, such as all these processes included in membrane separation require external energy input to remove the pollutants from wastewater. And apart from them, the membranes utilized in these processes are costly and are not reusable.

7.3.2 Advanced Chemical Oxidation

Conventional treatment techniques to remove PPCPs from wastewater are not that effective, so advanced chemical methods are required to handle these types of pollutants. Few of the advanced chemical methods are discussed in the following section.

7.3.2.1 Ozonation

Ozonation has a good potential to remove PPCPs from wastewater, and it is one of the most frequently studied oxidation processes. The method on which ozonation works is formation of hydroxyl radicals, and it strongly depends on the oxidizing capability of the hydroxyl radicals to remove PPCPs (Bai et al. 2016a, b), and therefore the amount of hydroxyl radicals generated becomes directly proportional to the rate at which the PPCPs get ozonized. This process is generally used in post-treatment of wastewater to remove PPCPs. More research is required to study the effect of various sources of wastewater on the formation of hydroxyl radicals, and also the release of toxic by-products of ozonation should be monitored.

7.3.2.2 Fenton Oxidation

Fenton oxidation is one of the oxidation methods to remove industrial wastewater pollutants with the use of iron salts and hydrogen peroxide at acidic pH. This method also heavily depends on oxidizing capabilities of the hydroxyl ions. Few studies have shown the effectiveness of this method to remove PPCPs. The fundamental process of Fenton oxidation is to use various metal catalysts to breakdown H_2O_2 to produce hydroxyl radicals (Xu and Wang 2012). More research is required to study the effect of various sources of wastewater on the formation of hydroxyl radicals, and also the release of toxic by-products of Fenton oxidation process.

7.3.2.3 UV Treatment

Recent studies have used UV treatment to remove PPCPs from wastewater (Kim et al. 2009). The principle behind the process of photolysis is to break the chemical bonds of the pollutants in the wastewater by applying direct UV light. But a study conducted by Vogna et al. (2004) had shown that photolysis by direct UV light is not that efficient for some of the pollutants such as carbamazepine. Yuan et al. (2016) has shown the effectiveness of UV treatment removal process, the UV light can be combined with hydrogen peroxide. This process is also based on generation of hydrogen radicals caused by the breakdown of hydrogen peroxide by UV light. More research should be done to study the efficiency of this process to remove different pollutants from wastewater with a mixture of complex pollutants.

7.3.2.4 Ionizing Radiation

A study conducted by Kim et al. (2014a, b) showed that radiation of gamma rays has a higher potential to degrade lincomycin, sulfamethoxazole, and tetracycline when present in aqueous environment. Another study conducted by Sági et al. (2016) showed that the BOD/COD value of sulfamethoxazole after treatment with gamma radiation at 2.5 kGy was improved. Kimura et al. (2012) used 2.0 kGy of gamma irradiation on wastewater to completely biodegrade stern PPCPs such as carbamazepine, ketoprofen, mefenamic acid, clofibric acid, and diclofenac. In the study conducted by Liu and Wong (2013), it was reported that when H_2O_2 was combined with gamma radiations, the removal efficiency of TOC was heavily increased from 5% to 48%.

7.4 Biological Treatment: Introduction

Recently, biological treatment of PPCPs has become one of the most researched areas for degrading persistent organic pollutants. This technique has several advantages over the existing physiochemical techniques such as easy operating parameters, recovery of additional by-products, and cost-effectiveness. In biological treatment process of PPCPs, the focus is mainly on factors which can increase the robustness of the process such as type of microbial culture to be used, material of the sorption process, and calculating the potential of degradation and also production and disposal of secondary pollutants with sludge. Various biological treatments have been described in the following section.

7.4.1 Aerobic Biological Treatment

7.4.1.1 Activated Sludge Process (ASP)

Activated sludge process (ASP) is one of the most frequently used techniques to treat PPCPs in wastewater treatment processes (WWTPs). This technique follows the principle of using synergistic microbial population to degrade PPCPS. Several studies have conducted experiment to increase the efficiency of biodegradation by allowing cultures of mixed microbes to grow in activated sludge (Zhou et al. 2014). While some of the population of these mixed microbial cultures feed on the PPCPs, others use certain biochemical pathways to degrade them, thereby making this treatment method one of the potential candidates to treat PPCPs in wastewater efficiently (He et al. 2020). Suarez et al. (2010) studied compounds such as trimethoprim, sulfamethoxazole, carbamazepine, and diazepam and showed that these compounds are highly resistant towards biological transformation. Verlicchi and Zambello (2014) studied the removal process of 29 antibiotics by using conventional activated sludge (CAS) system. This study reported biological transformation of most of the compounds, but spiramycin had an insignificant removal rate, while cefaclor showed a removal rate of around 98%.

7.4.1.2 Membrane Bioreactor (MBR)

Membrane bioreactor (MBR) is an alternate method for PPCPs removal, and it works with a combinational approach where membranes and ASP work together. This method uses ultrafiltration membrane rather than secondary sedimentation tank (Yang et al. 2019). A study conducted by Sahar et al. (2011) compared antibiotics such as macrolide and sulfonamide removal process between CAS and MBR techniques, and the data showed that 15–42% of the antibiotics were removed by MBR technique compared to CAS process. Compounds such as carbamazepine and EDTA which are effectively removed in CAS however get poorly removed in MBR, but other persistent compounds such as diclofenac and sulfophenyl carboxylates get easily removed through MBR technique (Hai et al. 2011). In a different study, it was showed that MBRs were efficient in removing 90% of the 23 PPCPs out of 26 PPCPs used. ECs such as atorvastatin, metformin, 2-hydroxyibuprofen, and naproxen were most effectively removed, whereas compounds such as meprobamate, clarithromycin, trimethoprim, and thiabendazole were not so significantly removed through this process (Kim et al. 2014a, b).

7.4.1.3 Sequencing Batch Reactor (SBR)

This technique requires choosing certain suitable organisms that have the capability to degrade and remove PPCPs from wastewater systems. The study conducted by Muz et al. (2014) used both oxic and anoxic conditions in lab-scale SBR units to remove PPCPs such as endocrine-disrupting compounds. The data showed that 80% of the PPCPs were removed without involvement of any nitrifying microbes, when the experiment was conducted at (solid retention time) SRT of 5 days. The result of this study also showed that the process of removing carbamazepine followed aggregation onto sludge, while the leftover PPCPs were removed through biodegradation.

PPCPs can also be degraded through aerobic granular sludge sequencing bioreactor (AGSBR). The technique makes use of extracellular polymeric substances (EPS) which are present on the outer surface of the bacterial cell. EPS are made up of proteins and polysaccharides which help in aggregation and formation of aerobic granular sludge. In a study when PPCPs such as prednisolone, ibuprofen, naproxen, sulfamethoxazole, and norfloxacin in synthetic wastewater were added to AGSBR, initially the amount of EPS increased, because to protect themselves from the toxic effect of these compounds, the microbes synthesized and exported out more EPS. But with duration of time, the content of EPS in AGSBR decreased because the EPS secreted by the microbes started combing with the PPCP compounds and this made free PPCP molecules less available in the wastewater which in turn reduced the toxicity these compounds pose to the microbes. Therefore, this technique is an excellent method to remove PPCPs from wastewater, but more studies involving research with real wastewater are required to estimate the full potential of this technique (Shi et al. 2013).

7.4.2 Natural Aerobic Treatment

7.4.2.1 Waste Stabilization Ponds (WSPs)

This method is also a budding candidate for PPCPs removal from wastewater. A study conducted by Li et al. (2013) had shown that WSPs have the capability to remove 88–100% of PPCPs at (hydraulic retention time) HRT of 20–30 days. Because this technique involves processes such as biodegradation, photodegradation, and sorption onto solids, they are highly effective to remove PPCPs from wastewater.

7.4.2.2 Constructed Wetlands (CW)

Recently CWs have become an attention for extraction of PPCPs from wastewater (Li et al. 2014). But parameters such as carbon load (CL) and hydraulic rate (HR) affect the efficiency of PPCPs removal (Sharif et al. 2014). A study done by Chen et al. (2015) showed that by utilizing integrated CWs, antibiotics can be removed from domestic wastewater. The rate of removal of the antibiotics was found to be 78–100%. More than 70% of the antibiotic compounds such as cotinine, nadolol, ciprofloxacin HCl, and enrofloxacin were efficiently removed; however, only 20–50% of the compounds were removed when it comes to persistent PPCPs such as salinomycin, monensin, and narasin. Further research should be conducted to evaluate the potential of these CWs to treat PPCPs in secondary wastewater treatment plants.

7.4.2.3 Microbial Cultures

Recent researches have shown that microbial cultures of pure strains collected from sediments and activated sludge after secondary treatment of wastewater can be effectively used for removing PPCPs such as sulfamethoxazole (Reis et al. 2014; Jiang et al. 2013), iopromide (Liu et al. 2013), ibuprofen (Almeida et al. 2013), paracetamol (De Gusseme et al. 2011), diclofenac (Hata et al. 2010), triclosan (Zhou et al. 2014), and carbamazepine (Santos et al. 2012). Reis et al. (2014) had shown that activated sludge harbors *Achromobacter denitrificans*, and when pure culture of this strain was used, it was able to effectively remove PPCPs such as sulfamethoxazole and other sulfonamides. Other studies have shown that cultures of *Delftia tsuruhatensis*, *Pseudomonas aeruginosa*, and *Stenotrophomonas* can effectively remove paracetamol. These microorganisms were not only capable of degrading the PPCPs, but they also used them as a carbon source for growth and survival (Almeida et al. 2013; De Gusseme et al. 2011). Currently extensive researches are being conducted on the usage of mixed microbial culture for removal and treatment of PPCPs from wastewater in WWTPs (Khunjar et al. 2011).

7.4.3 Anaerobic Removal Technologies

7.4.3.1 Bench-Scale Upflow Anaerobic Sludge Blanket (UASB)

A study conducted by Sponza and Demirden (2007) using UASB reactor in combination with continuous stirred tank reactor (CSTR) showed that PPCP such as sulfonamide (sulfamerazine) was removed effectively with 97% removal rate. Another study performed by Carballa et al. (2006) in mesophilic anaerobic conditions effectively removed ibuprofen and naproxen with a removal rate of 40% and 87%, respectively. For chemically alike compounds, removal rate of even more than 90% has also been achieved (Samaras et al. 2013). This technique is a bit superior when compared with aerobic processes when factors such as power input, generation of biogas, small area of installation, and cost-effectiveness are considered. But certain studies have also showed that this technique is not that efficient for removal of persistent PPCPs because of their diverse and complicated chemical composition (Deegan et al. 2011).

7.4.3.2 Upflow Anaerobic Stage Reactors (UASRs)

Chelliapan et al. (2006) conducted a research to study the extraction process of PPCPs from industrial wastewater utilizing UASRs and showed that the process is effective in removing high amount of PPCPs. In a different study conducted by Oktem et al. (2008) by combining both UASR and anaerobic filter technology, significant amount of COD was removed from wastewater containing high organic load. When thermophilic temperature was maintained in a study conducted by Sreekanth et al. (2009), it was reported that both COD and BOD were removed from organic load of 9 kg at a removal rate of 65–75% and 80–94%, respectively. But the study also revealed that PPCPs such as carbamazepine were not effectively removed by using UASR. In another work conducted by Carballa et al. (2006), anaerobic microbes from sewage sludge were used to remove PPCPs. While many of the compounds were effectively removed, iopromide and carbamazepine were found to be persistent.

7.5 Future Prospects and Conclusion

Currently since there are no legal restrictions on maximum permissible limits for the disposal of PPCPs in the environment, the amount of these compounds is rapidly building up in the environment. Although conventional treatment methods such as physical and chemical techniques are regularly used to degrade and remove PPCPs, it comes with some drawbacks such as they are not so eco-friendly and their cost of maintenance is very high. As many of these PPCPs are new emergent, knowledge about their fate, behavior, impact on the environment, and methods to treat them are very limited. So, future research should focus on improving the biological treatment methods by improving their degradation ability, lowering their power consumption, and reducing the release of secondary pollution.

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Genetic Engineering Strategies and Degradation of Pollutants Using Genetically Engineered Microorganisms (GEMs)

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Abstract

To keep the environment clean and safe, degradation of pollutants is a serious concern in the current scenario. Use of microorganisms in this regard is considered as a cost-effective and eco-friendly method. However, natural microorganisms have some limitations for degrading the harmful contaminants present in air, water, or soil. So, different enzymes have been expressed in microorganisms by genetic engineering. Such genetically engineered microorganisms (GEMs) are responsible for different degradative pathways like xenobiotics, heavy metals, organic molecules, etc. So far, different advanced molecular approaches (like rhizoremediation, protein engineering, metabolic engineering, etc.) and high-throughput studies (like metagenomics, transcriptomics, proteomics, etc.) have been performed to know more about the activities of these organisms. The production of harmless GEMs and their application in biodegradation of pollutants are discussed in this chapter.

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8.1 Introduction

Bioremediation consists of two parts: “bios” means life and refers to living organisms, and “to remediate” means solving a problem. “Bioremediate” refers to utilization of biological organisms to resolve environmental problems. Microorganisms are used to degrade pollutants and prevent the environment from pollution. In other words, it is a technology used to remove pollutants from the environment, thereby restoring the original natural surroundings and preventing further pollution (Sasikumar and Papinazath 2003). It can be simplified as the contaminated environment is decontaminated. Contaminants of the environment are cleaned up by using diverse metabolic abilities of the microorganisms, which helps convert the contaminants to harmless products by mineralization, generation of carbon(IV) oxide and water, or conversion into microbial biomass (Baggott 1993; Satyanarayana et al. 2012).

Bioremediation and biodegradation are often used equivalently. However, those are not the same. Bioremediation may include biodegradation as only one of the mechanisms involved in the bioremediation process. Biodegradable contaminants are always present in the wastes, and some microorganisms can degrade a fraction of contaminants (Walsh 1999). Therefore, it would be worth studying the biodegradation potential of the microorganisms. Over the century, microorganisms have been useful for removing waste and freeing the environment from pollution; thus bioremediation is contemplated as a relatively new technology for eco-friendly decontamination of polluted environments (Saeed et al. 2021; da Silva Vilar et al. 2021; Rafeeq et al. 2022). Among several applications of this technology, one is municipal wastewater treatment. The wastewater is microbiologically treated under specific conditions. Depending upon the metabolic activities of microorganisms, different systems of activated sludge and fixed films are applied (King et al. 1997) so that wastes and pollutants are permanently eradicated. Also, lasting potentials are excluded, taking advantage of less precious but more long-standing biological systems. Likewise, bioremediation approaches could be applied in a coalescent manner together and coupled with other treatment approaches. This is a natural process and thus perceived by the public as a good waste treatment process for polluted material resembling soil. Microorganisms suitable to degrade the contaminant increase in figures when the adulterant is present; when the adulterant is degraded, the biodegradation population declines. The remainders for the treatment are generally benign products and include carbon dioxide, water, and cell biomass. Common microorganisms generally sequestered from soil and water are *Alcaligenes*, *Microbacterium*, *Micrococcus*, *Methanospirillum*, *Aeromonas*, *Sphingomonas*, *Sphingobium*, *Rhodococcus*, *Aspergillus*, *Penicillium*, *Trichoderma*, *Streptomyces*, *Candida*, etc. (Zhao et al. 2017a, b; Mishra et al. 2021). Theoretically, there is enough bioremediation that can be applied against a broad range of adulterants, and bioremediation can be considered. Bioremediation can be regarded as a useful approach for the complete destruction of a wide variety of pollutants. Numerous compounds considered to be harmful and dangerous can be biotransformed to safe products.

Currently, contamination with different types of strong xenobiotics has become a major global problem. The degree of toxicity increases when an admixture of xenobiotics is present in a place, and it becomes a trouble to the terrain. The bioremediation process is an effective way to remove contaminants, as discussed before. But microorganisms fail to degrade pollutants when it is in admixture form. To solve this problem, researchers put different enzymes in microorganisms that are responsible for different degradative pathways. Those microorganisms are known as genetically engineered microorganisms (GEMs). Formulating an effective GEM, suitable for bioremediation, requires advanced molecular approaches, including the details about genes, metabolic pathways, and catabolic genes that are characterized for the degradation process (Liu et al. 2019; Bilal and Iqbal 2020). Recently, the power of different “omics” technologies like metagenomic, transcriptomics, and proteomics has been utilized to know more about the molecular details of bioremediation.

8.2 Molecular Approaches in Bioremediation

Naturally occurring microorganisms like bacteria and actinomycetes and other eukaryotic organisms like fungi or plants can degrade or detoxify hazardous substances which are harmful for human health and the environment as well. Despite the enormous catabolic potential incorporated within microorganisms for efficiently remediating wastes and other toxic by-products, the particular interactions between microorganisms like bacteria and pollutants do not always promote efficient remediation. Therefore, molecular approaches needed to be introduced to enhance the process of bioremediation.

The sophisticated metabolic techniques help to get a clear picture of bioremediation (including complex interactions) and many more advancements yet to be implemented in this field. Protein engineering and metabolic engineering have been the pioneers in the process of bioremediation. Furthermore, other methods including whole transcriptome profiling and proteomics have reached extensive use in bioremediation. With the advent of engineered strains, chromosomal integration of genes and rhizoremediation methods have spiked up greater potentials in this field of bioremediation.

An overview of the advanced molecular approaches associated with bioremediation has been presented below.

8.2.1 Rhizoremediation

Here, the pollutants are degraded by the bacteria, whereas the plant roots provide a suitable environment and critical nutrients to the microorganisms. The greater advantage to this form of bioremediation is that the plant roots offer a larger surface area for the bacteria to propagate, living within the system, and form biofilms along with providing the appropriate niche nutrients to the microorganisms, also helping the microorganisms to transport from the contaminated soil and facilitating oxygen exchange (Molina et al. 2018). On the other hand, bacteria should also adhere to the root cells and proliferate properly to promote the bioremediation process. Pollutants like chlorinated ethenes, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons, metals, fuels, and parathion can be neutralized via the rhizoremediation system (Kuiper et al. 2004).

8.2.2 Protein Engineering

Insights on DNA shuffling help to mimic the natural molecular evolution of genes promoting the efficient way of redesigning the DNA in concern. The DNA shuffling method is used to successfully construct a biocatalyst with higher degradation rates for chlorinated ethenes (trichloroethylene, 1,1-dichloroethylene, and trans-dichloroethylene) along with polycyclic aromatic hydrocarbons (naphthalene, phenanthrene, fluorene, and anthracene) (Canada et al. 2002).

Here, multiple mutations are incorporated to produce new enzymatic activity (Crameri and Stemmer 1995; Crameri et al. 1996). The method follows the steps as below:

1. Cleaving the gene with DNase generating DNA fragments (using PCR without oligo primers, thus reassembling a gene or a family of genes randomly from 10 to 300 bps using homologous recombination).
2. Extensions with dNTPs and polymerase.
3. Normal PCR and nested oligos used to produce the full-length gene with random mutations. These mutations arise due to PCR infidelity (polymerase base-reading errors) and the controlled insertion of mutated gene fragments. Thus DNA shuffling provides an efficient amount of mutations.

Following the above protein engineering method, saturation mutagenesis helps to develop new catalysts for bioremediation as it promotes site-directed mutagenesis. As a result, comprehensive information can be obtained, and drawbacks of random mutagenesis can be overcome (Sakamoto et al. 2001). Saturation mutagenesis, like DNA shuffling, needs a proper screening or selection method. A combination of DNA shuffling and saturation mutagenesis was used to create toluene-*o*-xylene monooxygenase from *Pseudomonas stutzeri* OX1 (Radice et al. 2006) for better degradation of chlorinated ethene and to identify novel residues for accelerating the degradation of *p*-nitrophenol (Vardar and Wood 2005).

8.2.3 Metabolic Engineering

It is a technique that aids the cell's metabolism (and only not just optimizing the desired enzyme) to achieve the desired specific goal using recombinant engineering (Bailey 1991), for example, metabolic engineering of *Pseudomonas* sp. B13, where five different catabolic pathways from three different bacteria were put together to promote the specific degradation of methyl benzoate and methyl phenols in a single organism (Rojo et al. 1987).

8.2.4 Whole Transcriptome Profiling

Like DNA profiling, this technique can determine the relative number of transcripts from the whole genome, which otherwise cannot be achieved by proteomics. Thus, it helps predict alterations in the protein formation by assuming the changes in transcription, particularly in prokaryotes (as regulation occurs at the transcription level). This technique also helps to identify the mutual relationships among the strains found in the rhizosphere, which are appropriate for bioremediation. The whole transcriptome study of bacteria and plants was done at first using *Erwinia chrysanthemi* on African violet leaves (Okinaka et al. 2002). A number of virulence genes were identified through that.

8.2.5 Proteomics

This technique goes along with transcriptome profiling, analyzing changes in metabolism via changes in the protein levels (i.e., originating from transcription-level changes). This technique holds the potential to promote bioremediation through metabolic engineering, for example, degradation of cis-1,2-dichloroethylene (cis-DCE) by metabolically engineered *E. coli* cells (Lee et al. 2006), as discussed earlier in Fig. 8.1.

8.3 Metagenomics

The word "metagenomics" is composed of two words, "meta" and "genomics." While "genomics" deals with DNA sequences, "meta" deals with the action of doing things together for many organisms. The term is used when microbial communities are examined and cannot easily separate one microbe from the other one. For example, when two bacteria are growing together and DNA sequences are collected from them, the bacteria's DNA sequence is assembled. Simply, it is the study of a collection of genetic material, i.e., genomes from a mixed community of organisms, particularly microbial communities. Most of the samples analyzed here are directly from the environmental communities.

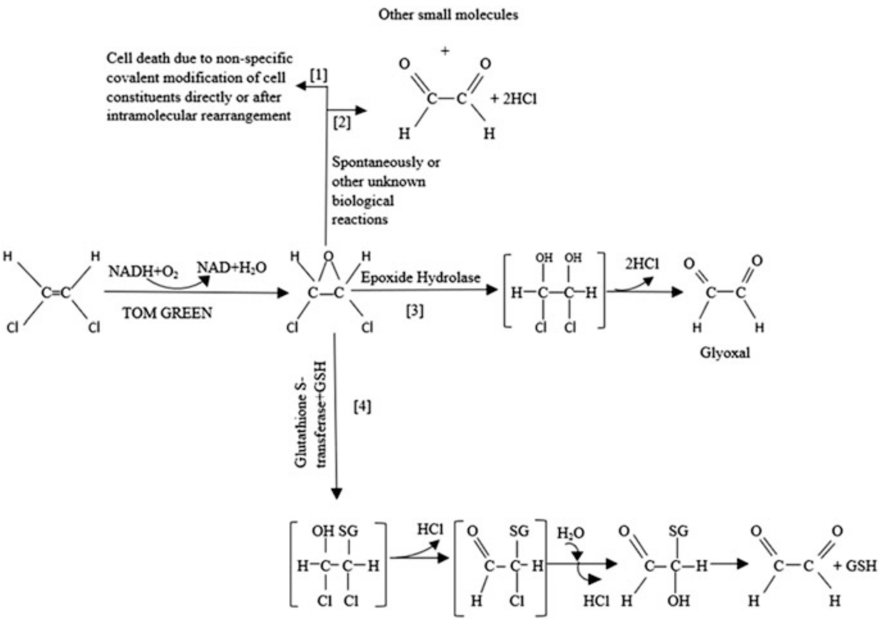

Fig. 8.1 Improved cis-dichloroethylene (cis-DCE) mineralization by cloning an evolved toluene *o*-monooxygenase (TOM-Green) to initiate the oxidation of cis-DCE (Rui et al. 2004a, b) in a following mechanism: possible spontaneous transformation of cis-DCE epoxide (steps 1 and 2) followed by two crucial detoxification strategies in which cis-DCE epoxide may be biologically converted by either an epoxide hydrolase (EchA) or glutathione *S*-transferase (IsoILR1) (steps 3 and 4)

Metagenomics offers a better way of understanding the microbial interactions that microbial genomics fails to comprehend. The invisible entities of a microbial community can differ enormously in their biochemical activities and interactions, not just between species but also within species. Analyzing the differences between contaminated and uncontaminated environments helps in the metagenomic study of all the bioremediating microbial communities. Metagenomics moves forward a long way in answering both the questions, concluding to view ecosystems themselves as biological units generating their genetic repertoires, in turn replacing the two different questions to properly ask “What is being done by the community?”

Metagenomics provides a better knowledge of the microbial communities in their niche. Complex ecological interactions involving dynamics of phage-host, lateral gene transfer, and metabolic complementation could be studied with precision using the approach of metagenomics. Different measurements, including the community composition, function rate, and dynamic activity, can be accessed and modeled in the environment with an active phase of microbial-genomic purpose. Hence, metagenomics provides a bridge to communicate natural cycles and human activities, which could make a good impact on the future shape of the planet.

8.3.1 Approaches of Metagenomics in Bioremediation

Pollution generated by the pollutants (i.e., natural and synthetic compounds) are some of the deadliest posed threats in human life and the ecosystems. A high-resolution genetic environment is needed to understand the interactions and the functioning of the contaminants and treatments affecting the complex microbial communities that live in natural environments. Complex biochemical networks within the microbial community help in the disintegration of environmental pollutants. So, the approach of using the bioremediating microorganisms to degrade off the hazardous pollutants is a promising one but only with the advent of new and appropriate high-throughput sequencing technology. A variety of metagenomics screening methods can be utilized in bioremediation studies to achieve a more accessible collection and analysis of targeted genomic information.

Phylotyping provides some reliable information about the species presence, but it cannot answer the exact activities performed by the intraspecific bacterial community. It would precisely tell us how much of the system's natural function has been deviated by contamination. Metagenomic data analysis would provide us with the pre- and post-contaminated differences based on their taxonomic and enzymatic diversity, provoking the search for potential active genes and associated organisms. Also, the adaptation to the nutrients, pH, temperature, carbon sources, oxygen, and water content is introduced within the contaminated sites to examine the responses of the microbial communities, being changed when subjected to a variety of environmental factors.

8.3.2 Types of Metagenomic Studies Used in Bioremediation

Metagenomic studies have led to a number of techniques whereby the information of all the communities or a whole-genome sample can be determined with precision.

Contaminated sites related to many studies have taken the help of gene-targeted metagenomics (Iwai et al. 2010), whereby particular gene regions are amplified, following which they are sequenced utilizing high-throughput technologies. This study has used this study to detect the specific functional genes (Bell et al. 2011; Iwai et al. 2010) and the 16S rRNA gene diversity (e.g., Bell et al. 2011; Gihring et al. 2011). The subjects of interest refer to the specific catabolic, reducing, or oxidizing genes in other bioremediation studies. A variety of screening methods are being used in bioremediation to optimize the information as an output shown in Table 8.1.

Degenerate primers help to amplify alkane monooxygenase genes obtained from hydrocarbon-contaminated soil. The cause took to a bacterium named *Alphaproteobacteria* which responded positively to changes with monoammonium phosphate (Bell et al. 2011). Amplicons were obtained from PCB-contaminated soil utilizing the degenerate primers aiming toluene/biphenyl dioxygenase genes and sequencing identified by a variety of novel dioxygenase gene clusters (Iwai et al. 2010). Bioremediation generally focuses on those microbial communities which most effectively degrade pollutants; thus, screening becomes much more critical.

Table 8.1 Screening methods and their scopes in bioremediation studies

S. No.	Contaminated substrates under various bioremediation treatments	Advantages	Disadvantages
1	Multiplexed 16S rRNA sequencing	(1) Can process many samples at low cost	(1) Horizontal gene transfer can make it difficult to pin functions to specific taxonomic groups (2) Primers bias against certain groups
2	Multiplexed gene-targeted sequencing	(1) Can process many samples at low cost	(1) Primers bias against unknown sequences
3	Screen substrates for bioremediation substrates	(1) Eliminates samples that are less effective at remediation (2) Allows greater sequencing depth for money available	(1) Omits potentially interesting information from less effective substrates
4	Screen DNA in plasmids for function	(1) Eliminates large stretches of DNA that are not involved in a specific process	(1) Requires that an entire pathway exists in one plasmid (2) Some gene products may be toxic to the host
5	Mixed culturing in vitro	(1) Population usually enriched in effective bioremediation of microorganisms	(1) Does not represent the natural system (2) Limited information on true ecology
6	Full metagenome analysis of all samples	(1) Most information possible	(1) High cost
		(2) Can perform any number of post hoc analyses	(2) Comprehensive databases are not available for many genes
		(3) Data available for future research	(3) Lots of data are ignored in the immediate study

Metagenomic studies were performed through the year-long time on the arctic soil that efficiently degraded the contaminating hydrocarbons in addition with an uncontaminated reference soil (Yergeau et al. 2012). Mixed culture studies helped to provoke the bioremediating potential in treatment facilities. With the help of such a concept, it was able to calculate the amount of branching in synthetic aromatic alkanoic acids giving rise to vastly mixed potential microbial communities (Johnson et al. 2011).

Plasmids like fosmids or cosmids having large genomic fragments gave an easy way of approaching the pre-screening of DNA. To practically search for genes having the capability of degrading catechol, metagenomic DNA from hydrocarbon-contaminated soil was disintegrated, cloned within fosmid vectors, transformed into *E. coli*, and plated with a carbon substrate—catechol. This experiment had some convincing results whereby an extradiol dioxygenase gene of a high diversity was observed along with a high density of 1 extradiol dioxygenase per 3.6 Mb of DNA being screened (Brennerova et al. 2009). A variety of metagenomic approaches are available for bioremediation researchers. Choice of technique practically depends on the questions being asked and resources being available. In a way, metagenomic approaches of more advanced molecular approaches could provide us with a detailed analysis of the contaminated sites along with more and more data being processed to help us understand the pollutant degrading bioremediating substance.

8.4 Transcriptomics

Transcriptomics can be defined as the study of transcriptomes. i.e., the whole set of RNA transcripts produced by a cell's genome. It can be assumed that the transcriptome is easier and simpler to study than the genome as only 3% of the human genome is transcribed as a gene, but it is reversed in reality because of the processes called alternative splicing and RNA editing, which enhance the complexity of transcriptomics. As a result of this process, each gene gives rise to many transcripts. A study of *Drosophila* Dscam gene (a homolog of human down syndrome molecule) revealed that nearly 40,000 different transcripts were produced due to alternative RNA splicing (Schmucker et al. 2000).

Previous study showed that a typical human cell expresses almost 15,000–20,000 different mRNAs of both with housekeeping and specialized functions. Some of these mRNAs will be splice variant forms of the same primary transcript, whereas some will be very abundant variants, a few will be moderately, and the remaining will be very rare. To find a revolutionized perspective of RNA expression in a cell, all of these transcripts should be quantified simultaneously. This requires a high-throughput assay which will give both sensitive and selective data parallelly (Liang 2013). Global transcriptome or RNA expression analysis is now based on two major strategies:

1. Direct sampling methods can analyze the sequences from target RNA populations or cDNA libraries or from sequence databases (Schnoor et al. 2004).
2. DNA array: works based on the protocol of hybridization analysis. But here, thousands of comprehensive, non-redundant libraries of DNA sequences on a support can be analyzed simultaneously (Schnoor et al. 2004).

Transcriptome analysis further helps in different studies, for example, the characterization of developmental stages of a cell, identification of the molecular mechanisms of a specific phenotype, identification of biomarkers which are differently expressed in disease condition, cancer studies, and also the establishment of the relationship between genetic variants and gene expression patterns associated with the diseases which in turn will highlight the origin of diseases (Schadt et al. 2005).

8.4.1 Transcriptomics in Bioremediation

Transcriptomics has a significant role in bioremediation more than any other "multi-omics" technology (Rawat and Rangarajan 2019). Bioremediation process of microorganisms is extensively studied nowadays with the help of transcriptomics. Regulation of gene expression studies (transcriptomics) illuminates the insight of microbial community at the molecular level so that molecular activity of microorganisms in a specific contaminated environment can be studied. These recent developments in research make bioremediation procedures more effective and active on a large scale. mRNA expression level (basically in the stress condition of every gene) can be determined by microarray technique, one of the major advancements of transcriptomic analysis. Such gene expression analysis in various environmental stress conditions gives information about regulatory proteins/conditions of the target organism. An analysis on *Bacillus subtilis* grown in vivo (under anaerobic conditions) reveals that more than 100 genes were affected when the stress condition was oxygen limitation (Singh and Nagaraj 2006). This DNA microarray data was analyzed by monitoring gene expression profiles of the *Bacillus subtilis*, both under normal environmental conditions and stress conditions. In stress conditions (oxygen limitation), it is observed that *Bacillus subtilis* can synthesize enzymes like alkane hydroxylase and alcohol dehydrogenase, which can degrade hydrocarbons. RNA sequencing analysis helped to find the gene and the specific strain of the bacteria, *Bacillus subtilis* strain A1. Also, these enzymes can degrade the C10–C14 compounds completely but are less efficient in degrading higher carbon compounds (Parthipan et al. 2017). To enhance the efficiency, the gene responsible for the bioremediation procedure is searched, and this data is used to modify the responsible gene accordingly.

Previous examples showed how microarray technology helps to find the exact gene responsible for bioremediation procedures. Hence sensitivity of microarray plays a huge part here. The higher the sensitivity, the more accurate the result will be. But some different parameters are needed as they play a vital role in validating DNA microarray's sensitivity since sensitivity often creates problems in PCR-based cDNA microarrays. The major reason behind this problem is that only those genes can be detected, contributing greater than 5% of the DNA community in a gene population. One such important optimal parameter is 5′-C6-amino-modified 70-mers. To monitor biodegradation pathways effectively, a 50-mer-based oligonucleotide microarray was created. It is shown that microflora of soil changed with different incubation conditions when naphthalene-amended enrichment was used. This data was analyzed effectively using a 50-mer-based oligonucleotide type of microarray (Cho and Tiedje 2002). Another transcriptomic analysis showed that a yeast *Cladophialophora immunda* could degrade toluene. Eight genes were identified which are responsible for toluene degradation. Though *Cladophialophora immunda* can degrade toluene, toluene triggers the fungus in the energy-saving state. Cellular metabolisms like respiration organic metabolism are affected by pollutants. If the expression of snoRNAs can be enhanced, then xenobiotics' negative effect. So genetic engineering methods help to express snoRNAs (Blasi et al. 2017). The transcriptomic study identified a gene of a bacterial strain *Stenotrophomonas bentonitica* BII-R7 with a uranium resistance mechanism. Upregulation of 148 and 185 genes was shown when exposure to 100 μM of uranium when cells were in lag and exponential phases. On the other hand, 143 and 194 genes were downregulated. In contrast, when 250 μM uranium was applied, 68 genes were upregulated, and 290 genes were downregulated in the lag phase. This limitation can be overcome by creating GEM (Pinel-Cabello et al. 2021). Another analysis proved that polycyclic aromatic hydrocarbon (PAH) can be degraded using a fungus *Dentipellis* sp. So, it is now widely used in the bioremediation procedure of PAH since it accumulates rapidly in the environment and is highly carcinogenic (Park et al. 2019). As PAH is very harmful to the environment, the efficiency of microorganisms in bioremediation needs to be enhanced so scientists took the help of genetic engineering. Enzymes like monooxygenase, dioxygenase, and hydro-aldolase degrade PAH. Every enzyme follows a different pathway. A variety of PAH-degrading gene clusters was put into a bacterium so that a wide range of PAH can be degraded simultaneously through different metabolic pathways (Wu et al. 2021). Thus, microarray becomes a promising tool that can solve environmental problems by in-depth understanding of bioremediation.

8.5 Proteomics

Proteomics is the scrutiny of the entire protein complement of a cell, body tissue, or organism under a specific set of conditions. It is the study of the complete proteome or the set of all proteins from an organism that performs the degree of quality and quantity of the synthesized proteins and their modulations under needed conditions. Proteins act as cellular factors which have the capability to control the function of a cell and its phenotypes further it can seize its functional state and dynamicity. The term proteomics was first discovered in the year 1997. The word proteome summarized protein and genome and was first coined by Mark Wilkins in 1994. Precisely, proteome is defined as the entire complement or database or full set of proteins that an organism has generated. The proteome is a broad term that includes certain changes or variations induced in a native protein when the microorganisms are subjected to various changes in diverse forms. As a principle, proteomics has extended its growth in the situations of physical interface interacting with those of biochemistry, computer wisdom, and bioinformatics with a broader extension of more significant issues and reduced user bias. Several technologies are used in different forms, but mainly they are used in coupled ways (i.e., one- or two-dimensional gel electrophoresis/mass spectrometry (MS) or liquid chromatography/MS). In every natural process, proteins are included, so after analyzing these proteins in the cell, it depicts that the active biological network is maintained with the help of biological interaction and cooperation. The cell responds to internal and external changes by controlling the position and activity of its proteins, so changes in the proteome, either qualitative or quantitative, give a shot of this supervisory network in action.

The proteome is a complicated dynamic body that can be defined as the composition of the sequence, structure, abundance, localization, modification, communication, and biochemical function of each of its factors, furnishing a precious and different data source. The study of the proteome leads to a number of implicit ethical issues, particularly those concerning the power of owner, storehouse, and use of tissues concerning human beings; the storehouse and use of data arising proteomic exploration (especially if this affects the privacy of the donor or could lead on to demarcation); the extent to which concurrence is needed; and questions concerning intellectual property and thus the exercises of human samples for proteomic exploration that generates a marketable product in the after stages. The analysis of the varied features of the proteome needs an inverse range of technologies and protocols for data integration and mining, which further clouds the difficulty of power of owner and intellectual property. Proteomics provides a way more robust and representative picture of the performing cell than other large-scale analysis, like genome sequencing or the worldwide analysis of gene expression; thus, the implicit ethical pitfalls associated with sample and data abuse are lesser.

8.5.1 Application of Proteomics in Bioremediation

In bioremediation, the major application of proteomics is to analyze the proper organization of membrane proteins. PAH is very harmful to the environment, and removal of PAH from the environment is a real problem, but using genetically engineered microorganisms, the bioremediation of PAH is now possible both in situ and ex situ. The insights of the proteins involved in the biodegradation of PAH need to be analyzed, and proteomics plays a major role in altering cell surface proteins and receptors (Sikkema et al. 1995). High-throughput methods like 2DE are used in the multidimensional protein identification technology (MudPIT) (Santos et al. 2004). For example, microorganisms like *Mycobacterium* sp. are pyrene degraders; it is observed that in the presence of pyrene, an 81 kDa protein catalase (peroxidase) is expressed in the genome of the particular strain, and this data was found using the 2DE method. Further experiments observed that another six proteins are overexpressed in the presence of phenanthrene, pyrene, and dibenzothiophene in the strain PYR-1 exposed to phenanthrene. Another high-throughput and modern technique, mass spectrometry, indicated the expression of another enzyme (hydroxylated dioxygenase) in the *Mycobacterium* strain 6PY1 in the pyrene environment. The protein and small molecules of peptides and proteins can be identified using mass spectrometry (Aebersold and Mann 2003). Modern proteomics analysis deals with advanced techniques like matrix-assisted laser disruption/ionization time-of-flight MS (MALDI-TOF-MS) and surface-enhanced laser-desorption-ionization MS (SELDI-TOF-MS), which will help to identify proteins and the structure and function of proteins responsible for biodegradation of xenobiotics which in turn helps to identify the molecular mechanisms and degradation pathways. Scientists use this biasless and non-redundant data to produce genetically modified organisms for the large-scale remedy of contaminants (Aebersold and Mann 2003; Landry 2002).

For example, the differentially expressed proteins were analyzed using SELDI-TOF-MS in blue exposed to PAHs and heavy metals (Knigge et al. 2004). Contaminants of water are now directly detected and identified by using the liquid chromatography MS (LC-MS).

8.6 GEMs for Enhanced Bioremediation

Genetically engineered microorganisms (GEMs) are organisms whose genetic composition has been changed using recombinant DNA technology like gene or cell technology to generate a character-specific efficient strain for bioremediation of soil, water bodies, and activated sludge by exhibiting enhanced degrading capabilities against a wide range of chemical contaminants that exert several toxic effects (Sayler and Ripp 2000). Such microorganisms have several advantages, e.g., they can survive under stress and can be used as bioremediator under various complex environmental conditions. Tools like horizontal gene transfer, cloning, electroporation, conjugation, and transformations are used to create successful GEM. Genetic engineering has led to the development of “microbial biosensors” to measure the degree of contamination in contaminated sites quickly and accurately. Various microbial biosensors nowadays are used to evaluate heavy metal concentrations like mercury, cadmium, nickel, copper, and arsenic (Verma and Singh 2005).

8.6.1 GEMs in Bioremediation

Genetic engineering method is a promising new tool for scientific advancement. Like other scientific studies, genetically engineered microorganisms revolutionized the field of bioremediation. Though microorganisms can naturally degrade xenobiotics, there are some limitations in natural bioremediation procedures like the following:

1. It is a prolonged procedure.
2. Xenobiotics present in the environment are not in a single form or a nutshell; it could be said that environmental pollution is a mixture of xenobiotics. Only a single microorganism cannot degrade all the xenobiotics present in the polluted area.
3. Xenobiotics can inhibit the growth of the microorganism.
4. The particulate matter of soil can absorb some xenobiotics. So microorganisms cannot get through the particulate matter and reach the xenobiotics present there.
5. Some xenobiotics are resistant to breakdown processes.

Because of these limitations, large-scale bioremediation procedures are not so easy. To overcome these problems, microorganisms have been genetically modified (Urgun-Demirtas et al. 2006). Genetic manipulation was done by transferring plasmids into bacteria with different genes for different degrading pathways. It

Table 8.2 A selected list of GEMs for xenobiotics degradation

GEMs	Xenobiotics	Ref.
Pseudomonas diminuta	Parathion	Serdar et al. (1982)
Pseudomonas oleovorans	Alkane	van Beilen et al. (1994)
Pseudomonas cepacia	2,4,5-Trichlorophenol	Wang et al. (2000)
Pseudomonas putida	Mono- and dichloroaromatic compounds	Samuel et al. (2014)
Alcaligenes sp.	2,4-Dichlorophenoxyacetic acid	McGhee and Burns (1995)
Acinetobacter sp.	4-Chlorobenzene	Breton-Deval et al. (2020)

was first done by an Indian scientist Dr. Ananda Mohan Chakrabarty in 1971. He successfully developed a new bacterium with different plasmids and named it superbug (*Pseudomonas* sp.). This bacterium was inserted with camphor-degrading plasmid (CAM) and octane-degrading plasmid (OCT). Although these two plasmids cannot coexist, homologous regions of DNA help in recombination and, finally, the formation of CAM-OCT plasmid. Using the same method, another strain was developed which contains xylene (XYL) and naphthalene (NPH) degrading plasmid, and these two bacterial strains were subjected to conjugation for the formation of a new strain called superbug with CAM-OCT and NPH-XYL plasmid (Pandey and Arora 2020). A few examples of GEMs that can degrade xenobiotics are presented in Table 8.2.

Other new approaches develop GEMs by gene manipulation. For example, GEM *Pseudomonas aeruginosa* was developed by scientist Ananda Mohan Chakrabarty which can produce a biosurfactant called glycolipid emulsifier which can remove the surface tension in oil and water interface, i.e., promotes bioremediation of oil (Chakrabarty 2010). Sodium dodecyl sulfate or SDS, a detergent compound, can be degraded by using a GEM *Pseudomonas* sp., strain MTCC (Ambily and Jisha 2014).

However, GEMs can enter the environment and form different health hazards and also can cause ecological disturbance, including the change in habitat. More research should be done on GEMs with good biosafety to overcome this associated risk. Thus, it can create wonders in the field of environment management.

8.6.2 Bioremediation of Heavy Metals

Heavy metals are the naturally occurring organic compounds found in the environment. With the excessive and inappropriate use of it, the biochemical and geochemical cycle is getting hampered, resulting in the release of heavy metals like cadmium, chromium, uranium, zinc, etc. into the natural resources like the soil aquatic environments. Continuous use and higher accumulation of such heavy metals can create health hazards on humans as well as on aquatic ecosystems.

Table 8.3 Sources and toxic effects of heavy metals on human health

Heavy metals	Sources	Toxic effects	EPA regulatory limit	Ref.
Cadmium	Paints and pigments, plastic stabilizers	Carcinogenic, mutagenic, kidney dysfunction, GI disorders, degenerative bone diseases	5.0	Salem et al. (2000), Degraeve (1981)
Chromium	Tanneries, steel industries, fly ash, electroplating	Hair loss, dermal diseases, GI disorders	0.1	Salem et al. (2000)
Copper	Pesticides, fertilizers, biosolids, ore mining and smelting	Liver cirrhosis, brain and kidney damage	1.3	Salem et al. (2000), Wuana and Okieimen (2011)
Mercury	Medical waste, electrical industries, coal combustion	Renal dysfunction, autoimmune disease, CNS injuries	2.0	Gulati et al. (2010)
Zinc	Steel processing, coal and waste combustion	Dizziness, fatigue, etc.	0.5	Hess and Schmid (2002)

8.6.2.1 Sources and Health Hazards of Heavy Metals

With the increase in the number of industries and anthropogenic activities, there has been a sudden increase in the disposal of industrial wastes in the environment, and also the use of agro-based chemicals results in the accumulation of heavy metals in the waterways and in the soil (Table 8.3). As heavy metals are non-biodegradable and persist for a long time, which can cause a long-lasting impact on the ecosystem, solutions are required to avoid heavy metal leaching. Many of them are toxic at a very low concentration, e.g., arsenic, cadmium, copper, mercury, lead, etc. are not only cytotoxic but are also carcinogenic and mutagenic. Hence several treatment technologies like chemical precipitation, oxidation/reduction, membrane filtration, and some other conventional technologies have been implemented to increase the efficiency, but as a result, they are expensive and also proved inefficient. So, this imperfection led us to use some plants and microorganisms like bacteria, fungi, algae, and yeast as biosorbents in the bioremediation of heavy metals to promote efficiency, economic feasibility, and also eco-friendliness.

8.6.2.2 Bioremediation by Adsorption with the Help of Microorganisms

Biosorption is a process that occurs naturally in certain biomass that concentrates some substances in them and also allows it to bind with contaminants onto its cellular structure. Microorganisms are omnipresent and react with heavy metals that are contaminated within the soil and waterways and convert these heavy metals into nontoxic forms. In bioremediation, the microorganisms can hydrolyze the organic contaminants to end products such as CO_2 and H_2O or to some intermediates that are primarily required by the microorganisms to enhance their cellular activity and for their cell growth. Biosorption is the process that requires the involvement of higher affinity of a biosorbent toward a sorbate (which are heavy metal ions) and continues until equilibrium is established between the two components (Das et al. 2008).

1. *Saccharomyces cerevisiae* acts as a potential biosorbent for the removal of Zn (II) and Cd(II) by using the ion exchange mechanism (Chen and Wang 2007). It also has been noticed that they can isolate up to 65–79% of Pb and Cd from the polluted soil (Damodaran et al. 2011).
2. *Cunninghamella elegans* is a promising organism against heavy metals which assists in decolorization and detoxification of textile wastewaters (Tigini et al. 2010).
3. The Indigenous strains of genus *Pseudomonas* AK1 and AK9 have been sequestered from the Ganga Basin, whose water is mainly contaminated with arsenic. This strain has biosorption efficiency toward heavy metals and also developed resistance toward arsenic and other heavy metals like silver (Ag), cadmium (Cd), mercury (Hg), and lead (Pb) (Satyapal et al. 2018).
4. Chromium is the most abundant element in the earth that mainly exists in two forms: trivalent (Cr^{3+}) and hexavalent (Cr^{6+}), where this hexavalent form is much more toxic, carcinogenic, and mutagenic (Bagchi et al. 2002). So, to reduce its toxicity and mobility, several microorganisms have been used, including *Rhizobium*, *Bacillus*, *Pseudomonas aeruginosa*, actinomycetes, *Escherichia coli*, *Vibrio harveyi*, *Alcaligenes*, *Enterobacter*, *Phanerochaete chrysosporium*, and *Shewanella*, which acts as an effective strategy to improve the quality of the effluent (Pal et al. 2005). Similarly, *Streptomyces rochei* ANH, a novel actinomycetes isolated from the Alexandrian Mediterranean Sea coast, Egypt, is an efficient biosorbent used to treat toxic heavy metals from the wastewater.

8.6.2.3 Bioremediation of Heavy Metals by Genetically Engineered Microorganisms

Nowadays, soil contaminated with heavy metals (HMs) and polycyclic aromatic hydrocarbons (PAHs) has become a worldwide concern environmental problem as it harms crop production, affects the soil's quality, and causes harmful health issues on humans via the food chain exposure. So, GEMs are introduced as a desired requirement. It has a higher bioremediation efficiency for soil contaminated with HMs and PAHs as it is eco-friendly and cost-effective (Table 8.4).

1. *Pseudomonas aeruginosa* is a genetically engineered microorganism which express a CadR protein (a Cd-specific binding protein) that showed an adsorption capacity of up to 131.9 μmol/g of Cd(II) (Tang et al. 2018).
2. The strain of genetically engineered *Pseudomonas fluorescens* HK44 has also been used to remediate soil contaminated with PAHs (Sayler and Ripp 2000).

Table 8.4 Genetically engineered bacteria for remediation of heavy metals

Heavy metals	Initial concentration (ppm)	Removal efficiency	Genetically engineered bacteria	Expressed genes	Ref.
Arsenic	0.05	100	*Escherichia coli* strain	Metalloregulatory protein ArsR	Kostal et al. (2004)
Cd^{2+}	–	–	*Escherichia coli* strain	SpPCS	Kang et al. (2007)
Cr^{6+}	1.4–1000	100	*Methylococcus capsulatus*	CrR	Al Hasin et al. (2010)
Cd^{2+}, Hg	–	–	*Ralstonia eutropha* CH34	merA	Valls et al. (2000)
			Deinococcus radiodurans		
Hg	7.4	96	*Escherichia coli* JM109	Hg^{2+} transporter	Zhao et al. (2005)

3. *Cupriavidus metallidurans* MSR33, a transconjugant strain, was engineered by expressing the IncP-1b plasmid, which contains the novel *mer*B, *mer*G, and other mer genes from the heavy metal-resistant strain of *C. metallidurans* CH34. This engineered strain exhibits as a broad-spectrum mercury resistance strain and can detoxify mercury from the polluted water (Rojas et al. 2011).

Anthropogenic and natural sources are the primary source of heavy metal pollution. Due to their non-biodegradable property and hazardous nature, such metals should be removed from the environment, for example, from soil and water bodies. Adopting an appropriate biosorbent in efficiency and economy is a major concern nowadays. Several conventional and biological remediation techniques have been used for the treatment, but they are mainly ineffective and have proven several drawbacks. Hence, genetically engineered microorganisms have been used vigorously to remove the contaminants as they are cost-effective and eco-friendly and provide a good efficiency potential. By several redox reactions, microorganisms can perform bioremediation processes including metal mobilization/immobilization. Industrial wastewater released into environmental segments, such as soil and rivers, requires immediate attention by governmental agencies, regular monitoring, and remediation using appropriate methods.

8.6.2.4 Biodegradation of Organic Pollutants

In recent years, the drastic increase in the organic pollutants in the environment has become a major concern which demands a proper treatment before their discharge into the ecosystem. Organic pollutants are subjected to the various physical and chemical treatment, but the entire process is hazardous for the environment because of the toxicity of the end products. Hence, the biological approach can be an alternative to treat the organic pollutant successfully for being cost-effective and nature friendly. The use of microorganisms and plants for mitigating polluted environments is rising as a promising and an appealing field of environmental biotechnology. Besides the use of whole-cell microorganisms, their extracellular and cell-free enzymes have also been considered as one of the innovative bioremediation techniques for same. Recent reports suggest that the effect of extracellular enzymes in the removal of pollutants is of greater advantage than the whole-cell microorganisms. This section, thus, will deal with various aspects and the potential application of both intracellular and cell-free enzymes in the bioremediation of the organic pollutants.

Organic pollutants are chemical compounds that consist of carbon and have a major negative impact on one or more components. Organic pollutants are broadly classified into three major classes that are as follows:

1. Hydrocarbon
2. Oxygen nitrogen and phosphorus compounds
3. Organometallic compound

The category includes hydrocarbons and related compounds like DDT, dioxins, and PAHs. They contain hydrogen besides elements of carbon. Some of them consist of chlorine and oxygen. There are a limited number of chemical bonds present, principally C-H, C-C, C-Cl, C=C, and C=C (aromatic). These bonds are relatively stable and have limited polarity, and this property is then conferred onto the related compounds.

In order to determine the overall fate of the compound, organic pollutants undergo various physical, chemical, and biological processes that act in an associated way in the environmental systems. There are many processes for the degradation of organic pollutants. Some techniques for the degradation of organic pollutants are listed below:

Physical Processes

Organic pollutants are degraded using physical processes, which has methods like photocatalytic degradation where Ag-modified Zn_2GeO_4 nanorods, TiO/graphene oxide nanocomposite hydrogels, biosilica coated with amorphous manganese oxide, etc. are used. These organic pollutants are decomposed through catalytic/photocatalytic oxidation, which is considered as one of the best ways of organic waste management.

Chemical Processes

In the chemical process, electrochemical dehalogenation of chlorinated benzene is carried out where chlorine is eliminated stepwise from the highly chlorinated benzene to get less chlorinated benzenes and transform to benzene.

Biological Processes

Soil, contaminated with organic pollutants, has issues like costly incineration and land disposal. Bioremediation provides a cost-effective treatment for those sites. Bioaugmentation, biostimulation, and bioattenuation are different types of biological processes, which are cost-effective.

8.7 Advantage of Microorganisms for Organic Pollutant Bioremediation

In recent decades, methodical studies have led to isolating a substantial array of organic compounds with new microbial strains. While microorganisms are comparatively unaccustomed to many organic compounds, they have evolved standby paths for their metabolism to reduce these contaminants. Microorganisms are the only organisms with a prodigious aptitude to exploit different organic/inorganic materials for burgeoning in the biosphere. Microorganisms can subsist in different ecological niches and perform unconventional metabolism and physiological behaviors. The bioremediation and biotransformation process aims to exploit the shocked, naturally occurring microbial catabolic variety of hydrocarbons (e.g., oils), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), radionuclides, and metals, to dissolve, convert, or absorb a broad range of a compound (Fig. 8.2).

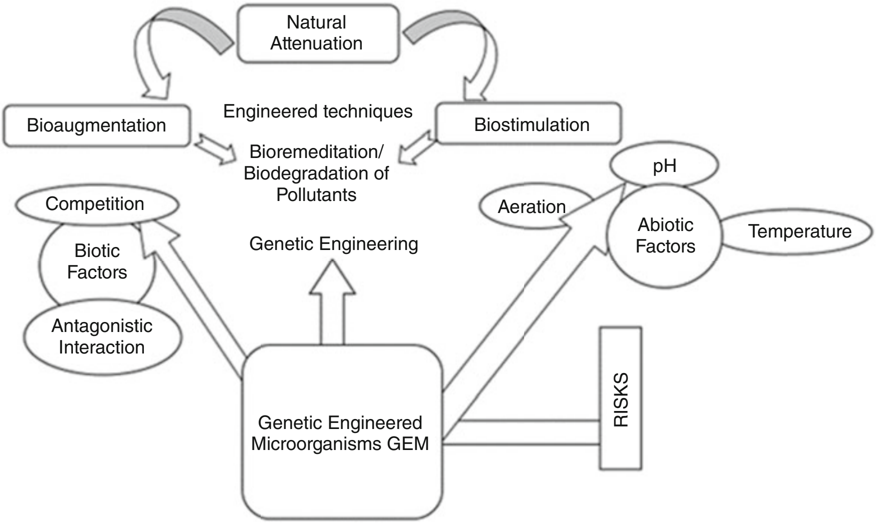

Fig. 8.2 Bioremediation of pollutants utilizing biodegradation abilities of microorganisms (Ratnakar et al. 2016)

8.8 Conclusion

The world's population is increasing day by day and thus the waste materials also. To get benefit from bioremediation technology at the fullest, the use of GEM-based technology is very much necessary. Such an interdisciplinary science depends on the variation of the substrates used by bioremediants in different types of aqueous and terrestrial habitats. One such organism is fungi, which has a high rate of biodiversity. They can be isolated from various environments and are potent groups of bioremediant. It is expected that genetically modified fungi will be more effective in the bioremediation of pollutants and wastes. With the help of cutting-edge techniques, this field of science will become more efficient in different environments, from battle fields to rural, urban, and industrial areas. Though the bioremediation with GEMs could be revolutionary, to date it is restricted in field application due to some limitations like its cost-effectiveness. Besides, GEM can enter the environment and cause harmful effects to living organisms and could be a reason to form multidrug-resistant microorganisms. However, the harmless GEM-mediated bioremediation is very much promising, and that day is not so far away. It is well expected that bioremediation with GEMs would expand to more specific scientific branches in the near future to quickly respond to the challenges of the current and future world.

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Biogenic Synthesis of Nanoparticles and Its Application in Wastewater Treatment

9

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Abstract

Nanotechnology is a boon in the field of science as well as for all life forms in our blue planet. These nanoparticles have found tremendous application in various fields such as in environmental biotechnology, in agriculture as fertilizers, in the production of glass and alloys and in solar cells, photoconductors, nanomedicine, cosmetics, food industry, drug delivery, biosensors, etc. Nanoparticles can be formed chemically, but recent research has focussed mainly in the production of

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nanoparticles by green/biogenic synthesis, which is found to be eco-friendly. Production of biogenic nanoparticles is very economical, utilizes less energy and produces little or no toxic end/by-products, so this method can be used as an alternative to other approaches. This book chapter highlights the various approaches and microbiological sources (such as bacteria, fungi, actinomycete, algae and yeast) for nanoparticle production and how their biosorptive and catalytic properties are used in the removal and degradation of various types of pollutants from the environment.

Keywords

Nanoparticle · Biological synthesis · Wastewater treatment · Biodegradation · Biosorption

9.1 Introduction

The presence of water in the Earth's atmosphere and in its crust originates from the world ocean's saline seawater, while freshwater represents just 2.5% of the aggregate. The absolute volume of water on Earth is assessed at 1.386 billion km^3 (333 million cubic miles), with 97.5% being salt water and 2.5% being freshwater. Of the freshwater, only 0.3% exist in liquid state on the surface (Gleick 1993). The expanding total world population, changing utilization patterns and improving living comforts and extension of irrigated agriculture are the principal driving forces for the rising worldwide demand for water (Vörösmarty et al. 2000; Ercin and Hoekstra 2014). The embodiment of worldwide water shortage is the geographic and temporal mismatch between freshwater request and accessibility. With the total populace anticipated to increment by an extra two billion (2×10^9) individuals, discovering ways to fulfil humankind's water requests while at the equivalent time securing the life support elements of freshwater systems currently positions among the most basic and difficult challenges of the twenty-first century (Postel 2000). It is now evident that alternative sources of freshwater are necessary to meet the current and future trend in freshwater demand. Nowadays, the primary focus is to manufacture freshwater with quality standards depending on specific use and mostly for human consumption purposes. For that reason, scientists are finding out new ways to treat wastewater either by physical, chemical or biological ways.

The various organic and inorganic pollutants from different sources such as textile, paper, chemical industries, agriculture runoff, municipal runoff, etc. contaminate the water heavily. These contaminants must be removed efficiently. To develop the sustainable use of water by removing these toxic contaminants efficiently is now one of the prime areas of interest for many researchers across the globe. In recent times, nanoparticles (a material whose diameter is between 1 and 100 nm) hold a promising significance of usefulness in various fields, starting from clinical wastewater treatment. There are enormous applications of nanoparticles not only due to their large surface area-to-volume ratio but also due to the presence of various properties such as optical, magnetic, conductive, catalytic, mechanical and adsorptive properties (Al-Hakkani 2020). There are mainly two approaches for the synthesis of nanoparticles, one is a top-down approach, where bulky materials are shredded into particles of small pieces irrespective of the control of atomic level initially, whereas in the bottom-up approach, smaller particles are self-assembled to produce the nanoparticles (Shah et al. 2015). But the conventional ways by which nanoparticles are synthesized are greatly replaced by the recent green synthesis approaches because there are various constraints in the older methods such as requirement of high temperature and pressure, high cost and the toxic effects of the chemicals used for their production (Sharma et al. 2019). Utilizing biogenic nanoparticles for wastewater treatment can be employed to provide safe and potable water.

Heavy metals are considered as potential harmful agents threatening life forms including our entire ecosystem, so removal of such dangerous pollutants from the environment is a must for healthy functioning of our ecosystem (Singh et al. 2010). Currently, there are various processes that are carried out for wastewater treatment such as ion exchange, membrane filtration and chemical precipitation. Among these processes, biosorption is a very eco-friendly, low-cost process for the safe removal of heavy metals, pharmaceutical compounds, dyes, detergents, etc. from the wastewater (Hua et al. 2012; Reddad et al. 2002). The process of adsorption also favours reusability of the adsorbents due to the presence of high surface area and lots of active sites (Liu et al. 2008).

In this review, our study focusses on the adsorptive property of the nanoparticles leading towards the process of wastewater treatment so that in the coming years the entire population around the globe gets safe consumable water for survival, thereby eliminating the problem of water scarcity. Here we have mainly portrayed the green synthesis method, a bottom-up approach, associated with the production of nanoparticles mostly the microbial sources such as bacteria, fungi, algae and yeast and its application in wastewater treatment. Such green synthesis methods are not only economical but also eco-friendly.

9.1.1 Advantages of Biogenic Synthesis of Nanoparticles

The most significant feature possessed by the green synthesized nanoparticles is the biocompatibility in nature and cost-effectivity (Baker et al. 2013; Li et al. 2011). The obtained biogenic nanoparticles are free from the contamination of the toxic by-products when compared with other methods (physiochemical and chemical synthesis of nanoparticles). Manufacturing nanoparticles from any biological source reduces the steps involved in their production, for example, there is no requirement of adding any functional groups on the surface of the nanoparticles (Baker et al. 2013). The presence of capping and stabilization agents present in the biological moieties eliminates the further addition of these external agents for the synthesis of biogenic nanoparticles (Makarov et al. 2014). This method of nanoparticle synthesis not only requires less energy but also is an eco-friendly approach. The synthesized nanoparticles have shown greater biosorption and catalytic activity due to their more specific surface area and unique properties. Mostly the microbial sources that are used for the production of nanoparticles can survive in different environmental conditions, i.e. different conditions of pH, temperature, pressure, aeration and so on (Rajasree and Suman 2012). The biomass is easy to handle, and scaling up of the biomass is also easy to perform. These biological nanoparticles are enormously used in the process of bioleaching, bioremediation, biomineralization, biomedical treatment and biocorrosion as many microbial strains that produce nanoparticles are tolerant towards high metal concentration.

9.2 Approaches for the Synthesis of Nanoparticles

There are two different approaches that are widely used nowadays for the synthesis of metallic nanoparticles:

1. Bottom-up approach: This approach is also referred to as self-assembly approach. It begins from the atomic level, followed by molecular level and finally performing clustering of all the levels. At first formation of nanoparticles takes place, and gradually various biological or chemical synthesis procedure is employed to assemble those nanoparticles into a final material. A major advantage of this process is that the chemical composition of the obtained nanoparticle is homogenous with lesser defects (Thakkar et al. 2010).
2. Top-down approach: This process begins with the size reduction of the starting material by applying any chemical or physical means. One of the main disadvantages of this method is the occurrence of defects in the surface structure, which eventually hampers the surface chemistry and physical properties of the nanoparticles (Thakkar et al. 2010).

9.2.1 Ways to Synthesize Biogenic Nanoparticles from Microbial Sources

Microorganisms are considered as major nanofactories due to their immense applications, eco-friendliness, less polydispersity, detoxification of heavy metals and many more. One such application of microorganisms is the synthesis of nanoparticles by making use of their supernatant, their biomass and their derived components. The nanoparticles produced by these microorganisms prevent aggregation of the nanoparticles thereby increasing its stability (Singh et al. 2016).

Nanoparticles are synthesized by microorganisms intracellularly or extracellularly. In intracellular synthesis, the microorganisms are incubated for a certain period of time in the presence of respective salt solution of metal (e.g. silver salt ($AgNO_3$) for silver (Ag) nanoparticles) where it has achieved an optimum growth, and then biomass is collected followed by centrifugation. The collected biomass is completely washed with sterile water, and then it is dissolved in a metal salt which is filter sterilized containing sterile water. Visual inspection of change in colour is a method to monitor the reaction mixture. When this incubation period gets over, the removal of the biomass is done by continual cycles of ultrasonication, followed by washing and finally by the process of centrifugation. After performing the above steps, it results in cell wall breakdown, thus facilitating release of the nanoparticles. To obtain the nanoparticles, centrifugation and washing of the final mixture are done. Similarly, in extracellular synthesis, the microorganisms are grown in optimum conditions of temperature, pH, etc. in the presence of desired salt solution of metal. Then the biomass is separated using centrifugation, and nanoparticles are collected in the supernatant. Finally, depending on the size of the nanoparticles, it can be collected as pellet from the supernatant by using high-speed centrifugation (Singh et al. 2016).

For example, cadmium sulphide semiconductor nanocrystals were produced by *Escherichia coli*, when the bacterium was incubated with sodium sulphide and cadmium chloride (Sweeney et al. 2004). When the bacterium entered into the stationary phase, a 20-fold increase in the yield was observed suggesting that growth phase of the microorganisms can influence the nanoparticles production. A non-magnetotactic bacteria *Acinetobacter* can synthesize magnetite nanoparticles in the presence of iron precursors and in aerobic conditions which exhibited excellent magnetic properties (Bharde et al. 2005). A work reported that the presence of *Clostridium thermoaceticum* precipitates CdS in the medium as well at the cell surface (Cunningham and Lundie Jr 1993).

Lengke et al. (2007) successfully synthesized Ag NPs by *Plectonema boryanum* UTEX 485, using nitrate as electron acceptor at 25 °C. Similarly, it was reported that the nitrate reductase enzyme was mainly responsible for the production of silver nanoparticles by *B. licheniformis* (Zhang et al. 2011). While Konishi et al. (2004) demonstrated optimum production of gold nanoparticles from *Shewanella* algae, a mesophilic bacterium using H_2 as an electron donor indicating that both the electron donors and acceptor play a significant role in the process. Similarly, optimization of pH is also important for the same as it can influence not only the shape and size of the nanoparticles but also the location, i.e. intracellular vs. extracellular. Another similar study showed that *Rhodopseudomonas capsulata* produces gold nanoparticles of different shapes and sizes over a range of pH from 7 to 4 incubated in aqueous chloroauric acid solution (Shiying et al. 2007). It was found that when pH was 4, nanoplates were produced, whereas spherical gold nanoparticles ranging from 10 to 20 mm were synthesized at pH 7.

9.2.2 Synthesis of Biogenic Nanoparticles from Various Sources

9.2.2.1 From Bacteria

Pseudomonas aeruginosa SNT1 is able to synthesize selenium both intracellularly and extracellularly after biotransforming oxyanions of selenium (Yadav et al. 2008). *Delftia acidovorans* can help in manufacturing gold nanoparticles due to the production of delftibactin (Johnston et al. 2013). *Escherichia coli* can produce zero-valent palladium nanoparticles on their cell envelope due to the presence of hydrogenases (Lloyd et al. 1998). *Pseudomonas stutzeri* can synthesize copper nanoparticles of spherical shape having size between 8 and 15 nm (Varshney et al. 2010). *Lactobacillus* strains from buttermilk are able to synthesize silver and gold nanoparticles intracellularly in large amounts (Nair and Pradeep 2002). Jayaseelan et al. (2012) have recently mentioned that zinc oxide nanoparticles were synthesized from *Aeromonas hydrophila* within 24 h when kept at room temperature. The spherical shaped nanoparticles with size ranging from 57 to 72 nm exhibited antimicrobial activity against two microorganisms, i.e. *Aspergillus flavus* and *Pseudomonas aeruginosa*. Synthesis of cobalt oxide nanoparticles from *Brevibacterium casei* was achieved when it was cultured for 1 day in a nutrient broth media containing beef extract-sodium chloride-peptone (Kumar et al. 2008). Zinc oxide nanoparticles can be synthesized from *Lactobacillus sporogenes*, a probiotic microorganism, at an acidic pH around 4–5 (Prasad et al. 2010). *Shewanella putrefaciens* can produce uranium oxide when grown in an aerobic condition in a tryptic soy broth for 24 h at a temperature of about 30 °C (Singer et al. 2009). *Serratia* sp. in Luria-Bertani broth medium can produce CuO (copper oxide(s)) nanoparticles at 37 °C for a period of 48 h (Saif Hasan et al. 2008).

9.2.2.2 From Fungi

Fungi are exploited nowadays for the production of nanoparticles because they are easy to scale up and have excellent metal bioaccumulation property; hence, they are efficient microfactories for green synthesis of nanoparticles as they are economical and easy to handle (Thakkar et al. 2010). A study using *Fusarium oxysporum* was performed by Uddin et al. (2008), and its report shows that this fungus which was grown at room temperature in a malt extract for 72 h at 28 °C containing glucose and peptone produced bismuth oxide nanoparticles, which further has undergone calcination process for 3 h at 400 °C. TEM images of the nanoparticles have shown their morphology as quasi-spherical with the average size of 5–8 nm. *Fusarium oxysporum* are also capable of synthesizing zirconia nanoparticles when cultured in MGYP medium containing ceraflux potassium zirconium fluoride at pH 3.6 at 27 °C when incubated for 72 h (Bansal et al. 2004). Magnetite ferric oxide nanoparticles were synthesized successfully by using *Fusarium oxysporum* and *Verticillium* sp. from $K_3[Fe(CN)_6]$ and $K_4[Fe\ (CN)_6]$ (Bharde et al. 2006). Vigneshwaran et al. (2007) showed that silver nanoparticles of 8.92 nm size accumulated on the cell surface of *Aspergillus flavus* in the presence of silver nitrate solution. *Colletotrichum* sp. was used by Shankar et al. (2003) for the production of zero-valent gold nanoparticles, having a size of 8–40 nm with a rod-like and flat disc-like structure. Kathiresan et al. (2009) isolated *P. fellutanum* from *Rhizophora annamalayana*, a mangrove root, which was successfully utilized to produce fungal-shaped silver nanoparticles within 24 h time having a size between 5 and 25 nm.

9.2.2.3 From Actinomycete

Ahmad et al. (2003a, b, c) demonstrated gold nanoparticles synthesis using *Rhodococcus* sp., an alkalotolerant actinomycete due to the presence of the reductase enzyme. The size of the nanoparticles was between 5 and 15 nm. Similarly, *Thermomonospora* sp. was also explored for the synthesis of gold nanoparticles (Ahmad et al. 2003a, b, c). The amide bands, originating from the *Thermomonospora* sp., worked as capping agents and helped them in stabilization and maintaining their size. Silva-Vinhote et al. (2017) worked with three different strains of *Streptomyces* sp. (DPUA 1549, DPUA 1747 and DPUA 1748) and were able to successfully produce silver nanoparticles having antimicrobial properties mostly against gram-positive bacteria. *Streptomyces griseoruber*, an actinomycete, was isolated from soil and exploited for the gold nanoparticle synthesis at 120 rpm at a temperature of about 24 °C. These synthesized gold nanoparticles were also able to degrade methylene blue showing its environmental application (Ranjitha and Rai 2017).

9.2.2.4 From Algae

Parial and Pal (2015) worked with *Rhizoclonium fontinale*, marine algae, for the synthesis of gold nanospheres. The highest yield of the gold nanospheres of size 16 nm was obtained at pH 9, when incubated with $(AuCl_4)^-$ for a period of 72 h. *Chlorococcum humicola* is a chlorophyte that can be used to produce spherical-shaped, 2–16 nm silver nanoparticles (Jena et al. 2013). Mahdavi et al. (2013) showed that *Sargassum muticum* were able to produce iron oxide (Fe_3O_4) nanoparticles of cubic shape at room temperature. Rahman et al. (2009) identified that *Phormidium* is an appropriate alga for the generation of copper nanoparticles extracellularly. Similarly, *Chlorella vulgaris* was explored for the production of palladium nanoparticles recently (Arsiya et al. 2017). The stability of the nanoparticles was conferred by the amide and polyol groups, originating from the algae. *Spirulina platensis* can be exploited for the production of bimetallic nanoparticles of silver and gold too. The algal culture was incubated with $AgNO_3$ and $HAuCl_4$ for 120 h at 37 °C, and silver nanoparticles (7–16 nm), gold nanoparticles (6–10 nm) and bimetallic silver-gold nanoparticles (17–25 nm) were produced successfully (Govindaraju et al. 2008).

9.2.2.5 From Yeast

Kowshik et al. (2002) performed differential thawing of a yeast strain MKY3 that is tolerant towards silver, to manufacture silver nanoparticles extracellularly of size 2–5 nm. Similarly, Jha et al. (2009) demonstrated *Saccharomyces cerevisiae* produced spherical-shaped antimony oxide nanoparticles, which showed semiconductor-like properties. The presence of oxidoreductases and quinines in the cytosol or membrane of *Saccharomyces cerevisiae* helped in the nanoparticle synthesis (Gericke and Pinches 2006a, b). A recent study focussed on the isolation of *Magnusiomyces ingens LH-F1* from sea mud for the synthesis of gold nanoparticles using hydrogen tetrachloroaurate(III) hydrate (Zhang et al. 2016). Visual indication of purple colour signifies the AuNPs formation. The gold nanoparticles obtained were of various shapes such as pentagon, triangle and hexagon, and few of them were irregularly shaped. The size of the nanoparticles ranged between 10 and 80 nm suggesting that reaction process needs to be optimized to control their shape and size

(Zhang et al. 2016). Recently, silver nanoparticles were synthesized successfully simply from *Saccharomyces cerevisiae*, baker's yeast, using silver nitrate as a metal ion precursor, indicating the simple yet cost-effective biosynthesis of various nanoparticles (Olobayotan and Akin-Osanaiye 2019). The formed AuNPs also exhibited antimicrobial activity.

9.3 Various Parameters Affecting Biosynthesis of Nanoparticles

Several factors can affect the synthesis of nanoparticles such as pH, temperature, contact time, salt concentration, mixing ratio, incubation period, redox conditions, aeration, etc. Konishi et al. (2004) showed that gold nanoparticles from *Shewanella* algae, a mesophilic bacterium, use H_2 as an electron donor. At pH of 7, the size of the gold nanoparticles was 10–20 nm, while it was larger in size (50–500 nm) at pH 1. Not only that, the location of the gold nanoparticles also changed from the periplasmic space to extracellular when pH changed from 7 to 1. Similarly, Gurunathan et al. (2009) found that *Escherichia coli* mostly produced silver nanoparticles when the pH was maintained at 10. The effect of temperature was clearly visible, when the synthesis of silver nanoparticles using *Trichoderma harzianum* was demonstrated by Ahluwalia et al. (2014). It shows that synthesis rate increased when temperature increased from 10 to 40 °C but decreased again thereafter. In a similar study of silver nanoparticles biosynthesis using *Colletotrichum* sp. ALF2-6, Azmath et al. (2016) also suggested that increasing the temperature helped in increasing the rate of synthesis, and 50 °C was the optimum temperature. On the other hand, it was reported by Obaid et al. (2017) that when the temperature was made at 10 or 80 °C, there was no synthesis of silver nanoparticles by *Rhizopus stolonifer* which may be due to the inactivation or denaturation of enzymes responsible for biosynthesis at these temperatures.

Yarrowia lipolytica NCIM 3589, a marine yeast, was explored successfully to produce gold nanoparticles (Agnihotri et al. 2009). It was suggested that different pH influenced the properties of the nanoparticles: when pH was 2.0, due to nucleation reaction, the colour was golden, while the colour changed to pink when the pH was 7.0, and further when the pH was changed to 9.0, the colour found was purple. In addition, Bharde et al. (2005) suggested that by using suitable iron precursors in the aqueous solution and under fully aerobic condition, the *Acinetobacter* were able to synthesize magnetite nanoparticles having excellent magnetic properties, while the rate of synthesis was much slower in the absence of air. Ahmad et al. (2003a, b, c) performed two different studies using *Thermomonospora* sp. and *Fusarium oxysporum* to produce monodisperse gold nanoparticles and suggested that an alkaline and slightly elevated temperature conditions favoured *Thermomonospora* sp. as compared to *Fusarium oxysporum* in the synthesis.

The quantity of biomass can also affect the nanoparticle synthesis rate. When the biomass concentration of *Penicillium oxalicum* was increased, it led to higher production of silver nanoparticles due to the release of higher nitrate reductase by the mycelium (Rose et al. 2019). Saxena et al. (2016) suggested the same, i.e. with the increase in biomass quantity of *Sclerotinia sclerotiorum*, the rate and production of silver nanoparticles also increased. Not only the biomass concentration but also other parameters like media, initial concentration of $AgNO_3$, pH and temperature also influenced the production and properties of silver nanoparticles, suggesting the need for optimization of the reaction parameters is very significant for the synthesis of nanoparticles (Saxena et al. 2016).

9.4 Application of Biogenic Nanoparticles in Wastewater Treatment

Water, the universal solvent, is the basic necessity for the functioning of all life forms (Goutam et al. 2018). Two-thirds of the Earth's surface is covered by water, but the addition of various organic and inorganic pollutants into the water either by natural or by anthropogenic activities degrades its quality as the result becomes harmful to the entire ecosystem (Bora and Dutta 2014). As per the latest report published in 2019 by WHO and UNICEF, all over the globe, 884 million or more people did not have safe water for consumption or drinking. The report also shows that more than 785 million people all around the globe did not have access to basic water services, and here comes the global challenge to provide clean and safe water for survival not only by managing water pollution but also by finding out various ways for wastewater treatment. Nanomaterials are now studied for water purification as well as for wastewater treatment due to its unique properties like high surface area, low price, less energy requirement, great mechanical properties and the most important its regeneration and reusability. Scientists are focussing more on biogenic nanomaterials in recent times for wastewater treatment as they are environmentally safer and economical compared to the chemically synthesized nanoparticles (Gautam et al. 2019; Mal et al. 2017; Mandeep 2020). Application of nanoparticles synthesized from microbial sources in wastewater treatment via adsorption has been described below (Table 9.1).

9.4.1 Biosorption of Pollutants

Rao et al. (2013) exploited the extract of *P. granum* and used it to synthesize iron nanoparticles. Surface modification of the nanoparticles was done by using two different strains of yeast *Y. lipolytica* (NCIM 3589 and NCIM 3590) in order to study the removal efficiency of Cr(IV) from the prepared solution. Removal efficiency was highest when the pH was 2.0 and the contact time was almost 60 min. With increase in temperature, the removal efficiency declined gradually. The maximum adsorption capacity of the nanoparticles modified with NCIM 3589 strain of *Y. lipolytica* was found to be 125.0 mg/g, whereas on the other hand, it was found that *Y. lipolytica* NCIM 3590 had maximum adsorption capacity of 156.3 mg/g suggesting that surface properties of the biogenic nanoparticles which generally depend on the

Table 9.1 Application of biogenic nanoparticles in pollutant removal

Biogenic source	Nanoparticle produced	Size (nm)	Shape	Removed pollutant	Reference
Serratia sp.	Hydroxyapatite	~25	Irregular	Phosphate	Yong et al. (2004)
M. ferrooxydans	Fe	100–130	Ropelike	As(III) and As(V)	Martínez-Cabanas et al. (2016)
P. aeruginosa JP-11	CdS	20–40	Spherical	Cd	Raj et al. (2016)
Anaerobic microbial consortium	Se	160–180	Spherical	Zn(II)	Jain et al. (2015)
S. thermolineatus	Fe	25	Distorted spherical	Cu	Kandasamy (2017)
C. freundii Y9	Se	–	Spherical	Hg^0	Wang et al. (2018)
Pseudomonas putida MnB1	Mn	8–9	Sticklike	Pb(II), Zn(II), Cd(II)	Zhou et al. (2015)
Pseudomonas sp. G7	MnOx			Tetracycline	Tian et al. (2018)
Bacillus sp.	Se	50–200	Spherical	MO	Ahluwalia et al. (2016)
Trichosporon montevideense WIN	Au	12–53	Spherical	2-nitrophenol, 3-nitrophenol, 4-nitrophenol, *o*-nitrophenylamine, *m*-nitrophenylamine	Shen et al. (2016)
Marine *Aspergillus terreus*	Se nanocrystals in upflow bioreactor	500	Nanostructures	Selenium	Raja et al. (2016)
Shewanella oneidensis MR-1	ZnS	5	Spherical	Rhodamine b	Xiao et al. (2015)
Geobacter sulfurreducens	Pd-BnM/H_2	–	–	Cr(VI)	Watts et al. (2015)
	Ag	25	Spherical	4-nitrophenol	

Cylindrocladium floridanum					Narayanan et al. (2013)
Desulfovibrio vulgaris	Bio-Pt	–	–	Ciprofloxacin, ibuprofen, sulfamethoxazole	Martins et al. (2017)
Trichoderma sp. WL-Go(ASS)	Au	20	Spherical	Acid Brilliant, Scarlet GR, Acid Red B, Acid Orange G, Acid Black 1, Reactive Red X-3B, Reactive Black, Reactive Red, Cation Red	Qu et al. (2017)
Stenotrophomonas maltophilia SelTE02	Se	160–250	Spherical	Selenite	Cremonini et al. (2018)

microorganisms are important for biosorption. Hence, selecting right microorganisms for biosynthesis of nanoparticles is a critical factor. Hennebel et al. (2011) suggested that when five different types of microorganisms such as *C. butyricum*, *C. braakii*, *K. pneumoniae*, *E. faecium* and *B. vulgatus* were cultured together, it leads to the production of palladium nanoparticles that are capable of degrading diatrizoate from wastewater compared to single microorganism. *Hypocrea lixii* and *Aspergillus aculeatus* both were successfully able to synthesize copper and nickel oxide nanoparticle, respectively, and both show strong biosorption activities (Salvadori et al. 2013, 2014).

Somu and Paul (2018) made ZnONPs using casein as a biogenic agent and used the nanoparticles to remove three metals and two dyes. The Pd(II) (194.93 mg/g) shows the maximum metal adsorption capacity followed by 156.74 mg/g and 67.93 mg/g for Cd(II) and Co(II), respectively. For dyes, it was 62.91 mg/g and 115.47 mg/g for Congo red and methylene blue, respectively, although it shows photodegradation of the dye as well. Yu et al. (2020) and their teammates worked with *Shewanella* cells in order to produce iron sulphide nanoparticles for the removal of chromium(IV). These nanoparticles were able to adsorb chromium(IV) having a capacity of 565.6 mg/g. *Serratia* sp. was used for producing biogenic nano-metered hydroxyapatite material (Bio-HAP). This Bio-HAP was 25 mm and acted as an efficient sorbent and removed Sr^{2+} (5.35 mg/g) from the simulated groundwater (Handley-Sidhu et al. 2011). *Serratia* sp. can also produce hydroxyapatite crystalline nanopowder successfully which adsorbed phosphate present in the wastewater (Yong et al. 2004). Iron oxide nanowires were produced by using *M. ferrooxydans* and worked excellently as nano-adsorbents to remove As(V) and As(III) (Andjelkovic et al. 2017). The reaction was greatly influenced by the pH and the oxidation state of the particular pollutant. When the pH was 3.0, it preferred the removal of As(V) ions, whereas at pH 6–10, removal of As(III) ions was preferred. The reported adsorption capacity at maximal level was 104.53 mg/g and 48.06 mg/g for As(III) and As(V) ions, respectively (Andjelkovic et al. 2017).

Kandasamy (2017) in a novel study with *Streptomyces thermolineatus* synthesized iron nanoparticles in a single step that were useful in removal of Cu ions from wastewater. Batch experiments showed 85% removal efficiency, and the data well fitted the pseudo-second-order kinetic model. Hexagonal shaped manganese oxide nanoparticles synthesized using *P. putida* MnB and removal of three different metal ions such as Pb(II), Cd(II) and Zn(II) was demonstrated by Zhou et al. (2015). Removal of Pb(II) was higher and quicker when compared with Zn(II) and Cd(II). pH and temperature were directly proportional to the removal efficiency. The greater the pH and temperature, the greater was the removal efficiency (Zhou et al. 2015).

9.4.2 Catalytic Applications of Biogenic NPs

The catalytic performance of NPs in degradation of organic water pollutants strongly depends upon their chemical and electronic structure. Principally, either electron donors or acceptors are employed for activating the catalyst which further degrades the pollutant through either reductive or oxidative pathways (Bhatt et al. 2021; Liu et al. 2020; Xiao et al. 2018). In fact, in the past few decades, nanotechnology-driven photocatalysis has been emerged as the most promising technique for degradation of organic water pollutants. Thereby, performance of biogenic NP-based photocatalysts has also been extensively studied in recent times. Often UV radiation is used for the excitation of such photocatalysts. However, solar energy can also be used for the purpose, but this demands synchronization of all contributing factors like electronic structure of catalyst, pollutant and tuning with other chemical species present in the wastewater. In a basic scheme of conventional catalytic degradation mechanism, the biogenic NPs involve the transfer of electrons from donor molecules to acceptor molecules and hence cause degradation of pollutants through either oxidative or reductive pathways. The surface functionalization of biogenic NPs in the form of phytochemicals attached to the surface are highly decisive in the course, as they not only contribute to stabilization of biogenic NPs and participate in the accumulation of reactants at the surface of the catalyst. This accumulation of reactants on the catalyst surface is extremely important for efficiency and sustainability of the technique (Alharbi et al. 2020; Srivastava et al. 2021; Varma et al. 2020).

For example, Susan Punnoose et al. (2021) have fabricated AuNPs via microwave-assisted one pot synthesis process using the leaves of *Myristica fragrans* for catalytic degradation of 4-nitrophenol and methyl orange dye using $NaBH_4$ (Fig. 9.1). The reductive degradation of 4-nitrophenol occurs very rapidly in the presence of the AuNP-based catalyst, while no such degradation was observed with $NaBH_4$ alone. This is due to the fact that the large kinetic barrier, which decreases the feasibility of reaction between donor and acceptor molecules, is bridged by the AuNPs. The degradation mechanism involves transfer of electrons from $NaBH_4$ to the active catalyst. Importantly, the phytochemicals attached to the surface of AuNPs attract the reactant molecules towards the surface via electrostatic interactions and facilitate the reduction process. The equilibrium degradation time for 4-nitrophenol at 0.02 mg/mL concentration was around 14 min. The studies showed that the pseudo-first-order kinetics was followed by a degradation process. Similarly, in

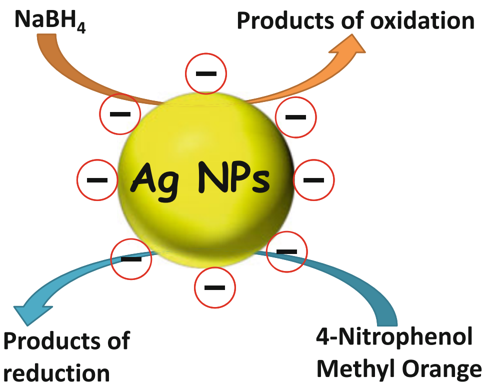

Fig. 9.1 Schematic representation of degradation process of 4-nitrophenol and methyl orange

degradation of methyl oranges, also biogenic AuNPs act as mediating catalysts for electron transfer from $NaBH_4$ to methyl orange. In addition to phytochemicals, the degradation activities of biogenic NPs also depend heavily on their size. In a report by Nguyen et al. (2020), biogenic Ag NPs which are synthesized through a novel and environmental friendly route using the aqueous extracts of *Stereospermum binhchauensis* and *Jasminum subtriplinerve* exhibited size-dependent degradation activity for 4-nitrophenol and methyl orange.

It has been depicted that the NPs obtained from *Stereospermum binhchauensis* leaves have size around 20 nm and a rate constant of 4.2×10^{-3} s^{-1} mg^{-1} and 7.3×10^{-3} s^{-1} mg^{-1} for degradation of 4-nitrophenol and methyl, respectively. But 8 nm Ag NPs are obtained in case of *Jasminum subtriplinerve* leaves, and these particles have degradation constant of 18.2×10^{-3} s^{-1} mg^{-1} and 12.6×10^{-3} s^{-1} mg^{-1} for 4-nitrophenol and methyl, respectively. Similarly, Zhang and Hu (2018) synthesized Pd and Au nanoparticles using *Bacillus* sp. GP and demonstrated enhanced catalytic degradation and removal of 4-nitrophenol.

Beside surface functionalities, other parameters like pH of wastewater and surface area of catalyst also govern the catalytic performance. Hennebel et al. (2010) demonstrated the utilization of biogenic Pd NPs in treatment of pharmaceutical wastewater in membrane technology. It was revealed that the pH conditions alter the surface properties of the catalyst. If pH is less than the pH_{pzc}, then the catalyst surface acquires positive charge and hence interacts strongly with anionic pollutants, whereas if pH is more than the pH_{pzc}, then the catalyst surface becomes negatively charged and starts interacting with cationic pollutants. Moreover, the report showed that biogenic NPs produce in situ biohydrogen and support the dehalogenation mechanism. Apart from surface functionalities, larger catalytic surface area is also imperative as it provides adsorption sites for donor-acceptor moieties.

Owing to their unique optoelectronic properties, the biogenic NPs also exhibited sustainable potential in photocatalysis of water pollutants. The plasmon bands and surface effects are used for characterizing the photocatalytic behaviour of biogenic NPs. In aquatic systems, they generate reactive oxygen species like anionic oxygen radicals and hydroxyl radicals after absorbing the radiation of appropriate wavelength. These reactive oxygen species are widely known for their interaction with organic water pollutants (both saturated and unsaturated compounds) and decomposition of toxic and complex pollutants into relatively non-toxic and simpler molecules. Importantly, in many cases the complete mineralization of water pollutants was also revealed (Chen et al. 2019; Kaplan et al. 2016; Khan and Cho 2019).

Since photocatalysis is a surface phenomenon, therefore, capping functionalities (phytochemicals) generated on the surface of NPs during their synthesis have a major role to play in photocatalytic efficiency. These surface functionalities mediate transfer of charge carriers from NPs to the dissolved oxygen or water molecules adsorbed on the surface of the photocatalyst to produce reactive oxygen species. However, in many conventional NPs, it has been seen that the capping functionalities sometimes compete with oxygen and water molecules for charge carriers, but such findings are not common in case of biogenic NPs. Furthermore, less experimental data is available on the roles of additional chemical species of biogenic origin on the surface of NPs in their photocatalytic activity. Currently, the formation of charge carriers after absorption of appropriate energy radiation by photocatalyst is the widely accepted mechanism that triggers degradation processes. Considering this, it can be concluded that the presence of layers of extra materials like proteins on the biogenic NPs may suppress their photocatalytic potential. In most of the literature reports, organic dyes are utilized as target pollutants for exploring the photocatalytic activities of biogenic NPs. However, not that much attention is paid in testing the capabilities of biogenic NPs for photocatalytic degradation of pharmaceutical wastes, pesticides, polyfluoroalkyl substances, etc. This can be attributed to the fact that it is easy to trace discolouration of dye during degradation. Moreover, it is worth much to explore decomposition mechanisms, nature of side products, reaction kinetics and mineralization for above-mentioned pollutants (Metz et al. 2015; Mughal et al. 2021; Sarmah et al. 2019). A number of biogenic NPs have been proposed for photocatalytic degradation of water pollutants till date, and some of them are given in Table 9.1.

In recent times, the photocatalytic abilities of biogenic NPs are also explored in inactivation of microorganisms. However, only Ag NPs and their derivatives are mostly evaluated for antibacterial activity. The different types of gram-positive and gram-negative species are used as target species. In certain reports, the antibacterial activity of other biogenic NPs like Cu, Ti, Zn, Fe and Mn has also been revealed. The mechanism of antibacterial activity involves oxidative and non-oxidative stress and metal ion release (Hossain et al. 2019; Majoumouo et al. 2019; Singh et al. 2018a, b).

Panchal et al. (2020) reported Ag-deposited ZnO using *Ocimum tenuiflorum* seed extract for inactivation of *E. coli*. The authors showed the release of a higher amount of reactive oxygen species in the case of Ag/ZnO compared to bare ZnO under irradiation of solar energy. This is due to a decrease in charge carrier recombination rate and tuned band gap that results in more absorption of solar energy after deposition of Ag. The apex-level performance of biogenic NPs has been shown by Singh et al. (2020). They revealed the role of biogenic NPs in controlling antibiotic-resistant bacterial infections. They revealed that biogenic Ag, Fe and AuNPs have unique physicochemical characteristics and undergo interactions with important cellular organelles and other biomolecules. Moreover, they can cause comprehensive changes in cell membrane permeability, oxidative stresses and other such events. Under such an environment, development of inherent resistance in bacteria against biogenic NPs is quite rare. Table 9.2 comprises some of the biogenic NPs that have been used for photocatalytic antibacterial activity.

Although biogenic NPs have shown tremendous potential in catalytic application for wastewater remediation, there are many challenging issues in their sustainability and commercial viability. The first is that there is a wide knowledge gap as far as their mechanism of degradation concerns. More in-depth investigations are required to properly probe their performance against different types of pollutants, degradation mechanism, cytotoxicity of by-products, degradation efficiency, etc. Secondly, the bulk synthesis protocols need to be designed as real-time applications require a large

Table 9.2 Biogenic nanomaterials for photocatalytic degradation of organic pollutants

S. No.	Biogenic nanomaterial	Targeted organic pollutant	Ref.
1.	Ag/ZnO nanocomposites from *Ocimum tenuiflorum*	Methylene blue	Panchal et al. (2020)
2.	Cu nanoparticles from *Escherichia* sp.	Azo dyes/textile wastewater	Noman et al. (2020)
3.	ZnO and CuO NPs from *Ferulago angulata*	Rhodamine B	Shayegan Mehr et al. (2018)
4.	TiO_2-C-O nanohybrids using *Capsicum annuum* L.	Methylene blue and 4-chlorophenol	Rajeswari et al. (2018)
5.	CdSe quantum dots (QDs) from *Rhodotorula mucilaginosa*	Malachite green	Cao et al. (2020)
6.	Ag NPs from *Streblus asper*	Methylene blue and 4-nitrophenol	Das et al. (2018)

Table 9.3 Biogenic nanomaterials for the antimicrobial and disinfection activity

S. No.	Biogenic nanomaterial	Microbial stain	Ref.
1.	Ag NPs from *Helicteres isora* root extract	*E. coli*, *V. cholera*, *S. typhi*, *P. aeruginosa*, *B. subtilis*, *M. luteus*	Bhakya et al. (2016)
2.	Ag/ZnO nanocomposites from *Ocimum tenuiflorum*	*E. coli*	Panchal et al. (2020)
3.	NiO from *Limonia acidissima*	*E. coli*, *S. aureus*, *P. aeruginosa*, *K. pneumoniae*	Kannan et al. (2020)
4.	Mn NPs from *Cinnamomum verum* bark extracts	*S. aureus*, *E. coli*	Kamran et al. (2019)
5.	CuO NPs from *Abutilon indicum*	*E. coli*, *Klebsiella*, *B. subtilis*, *S. aureus*, *R. mucilaginosa*	Ijaz et al. (2017)
6.	Ag NPs from *Streblus asper*	*E. coli*	Das et al. (2018)

amount of the active catalyst. Lastly, establishment of pilot-scale projects is needed for exploring the catalytic performance of the biogenic NPs (Table 9.3).

9.5 Conclusions

Water scarcity is a burning issue all over the globe. The availability of safe drinking water for consumption is decreasing day by day, so to resolve this issue, researchers and scientists all around the globe are focussing on various water treatment processes for producing high-quality clean drinking water. Nanotechnology-based approaches for wastewater treatment and purification are gaining significant attention nowadays.

The existence of various characterization techniques such as XRD, FTIR, UV-Vis, FE-SEM and so on has greatly helped in the confirmation of synthesis of nanoparticles as well as to analyse their optical and structural properties. Use of biogenic nanoparticles for water purification has proved to be greener and eco-friendly for the environment. Nanomaterials of biological origin can easily absorb various pollutants such as heavy metals, dyes, pharmaceutical compounds, etc. from the contaminated wastewater and eventually remove it and help us to purify the wastewater. Some of the biogenic nanoparticles can be recycled and reused for more than two times. Some of the bioinspired nanoparticles can function in a wide range of temperature and pH range without hampering its catalytic or sorptive property. Few experiments have also reported that biogenic nanomaterials have the potential to remove multicomponent solutions of water contaminants; this function can be used in membrane bioreactors in a water purification device to minimize dangerous pollutants in domestic water supply systems. Few challenges that are being faced in the production of biogenic nanoparticles are size control, aggregation and stability. Till now, there are a huge number of living organisms like plants, algae, fungi and bacterial species to be explored for the production and utilization of the nanoparticles and optimization studies. Specificity, cost-effectiveness, reusability, yield and stability are the major parameters of biogenic nanoparticle synthesis, and those are needed to be monitored cautiously.

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Biotechnological Approach for Treatment of Sludge from Municipal and Industrial Wastewater Treatment Plant

10

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Abstract

The wastewater treatment process is conducted to remove physical, chemical, and biological pollutants in the form of solids from wastewater streams. Municipal and industrial wastewater treatment plants reduce the amount of sludge entering landfills and adopt alternate methods through biotechnological processing (eco-friendly way) to create a sustainable environment. Anaerobic digestion (AD) process is one of the stabilizing biological processes as it can reduce the organic fraction and pathogen and also helps to produce biogas renewable energy. The interest of biochemical products (biohydrogen, enzymes, biopolymers (PHA), etc.) production from organic waste and sludge is increasing day by

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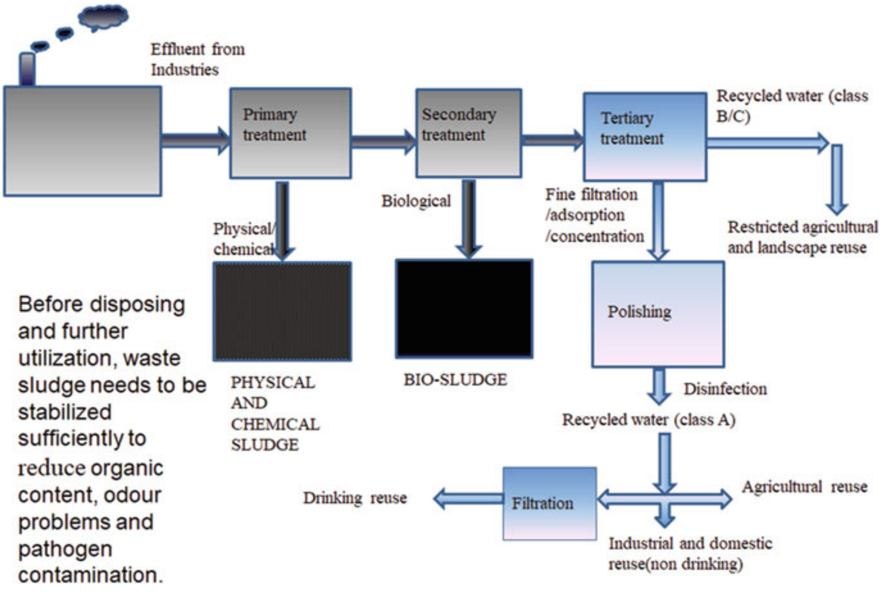
day. Among biofuels, biohydrogen has received more attention all over the world because it will satisfy the basic worldwide environmental protection and sustainable development.

Keywords

Sludge · Eco-friendly process · Anaerobic digestion process · Biohydrogen · PHAs

10.1 Introduction

In recent decades, due to rapid increase in population and industrialization, generation of wastewater increases in enormous amount. Untreated wastewater generally has high levels of biodegradable organic substances, nutrients, huge number of pathogenic microorganisms, and toxic substances. Such wastewater disposed to river or land area may generate unpleasant odour and increase the disease-causing organisms affecting the human health and other living organisms (Baier and Schmidheiny 1997). The ultimate goal of wastewater treatment plants is used to achieve the permissible limit for discharge of wastewater stipulated by environmental conservation and protection organizations like WHO (World Health Organization), pollution control boards, etc. Wastewater quality may be defined by its physical, chemical, and biological characteristics. Solids may be further subdivided into suspended and dissolved solids as well as organic (volatile) and inorganic



Before disposing and further utilization, waste sludge needs to be stabilized sufficiently to reduce organic content, odour problems and pathogen contamination.

Fig. 10.1 General wastewater treatment plant (fixed) fractions (Batstone et al. 2009). In that context, different phase of wastewater treatment process is conducted to remove physical, chemical, and biological pollutants from wastewater streams (Fig. 10.1).

Domestic, municipal, and industrial wastewater contain large quantity of dissolved solids which can be removed from them using biological treatment (aerobic or anaerobic) process. Among them, aerobic biological treatment (activated sludge process) process is commonly adopted by industrial and domestic wastewater treatment plant. Due to an increase in biological wastewater treatment plants, the generation of waste activated sludge from them also increased significantly (Bougrier et al. 2008). The incineration and landfilling are the most common methods used to dispose sludge from wastewater treatment plants. On one hand, the disposal of sludge by landfill is not a virtuous practice because chemical content in leachate coming off landfill creates the risk of groundwater contamination. On the other hand, it generates methane gas, which in turn increases the global warming by trapping and reflecting back huge amount of heat. Incineration of sludge is not an appreciable option because it releases carbon and nitrogen oxides into the atmosphere which in turn increase the global warming and climatic change (Bujoczek et al. 2000). Since, recent legislation in the developing countries is forcing the municipal and industrial wastewater treatment plants to reduce the amount of sludge entering landfills and adopting alternate methods to increase the recycling and recovery of products from sludge through biotechnological processing (eco-friendly way) to create a sustainable environment.

10.2 Sludge Classification

The development of wastewater treatment technology together with the implementation of stringent environmental legislation has successfully protected the water system from pollution in many of the countries of the world. However, at the same time, sludge is generated in huge amount from wastewater treatment plant. Sludge is an unwanted and unavoidable by-product generated from sedimentation process before and after the biotreatment process. Accordingly, the sludge are classified into three major types, namely, primary sludge, waste activated sludge (or secondary sludge), and tertiary sludge (Ødegaard et al. 2002). Tertiary sludge is produced during tertiary or polishing treatment of the biologically treated wastewater. Although the quantity of tertiary sludge is relatively less when compared with primary and secondary sludge and tertiary sludge contain only a very small fraction of organic solids, this type of sludge is often ignored for future treatment. Primary sludge is of a non-homogeneous nature because of some rather coarse constituents in it. After thickening in the primary settling tank, the solid content is about 5–10%, of which about 70% consists of organic matter. Wastewater normally contains thousands of different organics, so the composition of primary sludge is very complex (Liu et al. 2010). Secondary sludge or waste activated sludge (WAS) from the aeration tanks or humus from the trickling filters is composed of microorganisms and other life forms, which are withdrawn or flushed out of the system. The solid concentration in secondary sludge is about 1–6%, in which the organic fraction is also around 70% (Lafitte and Forster 2002). WAS consists largely of biological mass, mainly protein (30%), carbohydrate (40%), and lipids (30%) in particulate form (Lin et al. 1999).

10.3 Sludge Stabilization

Sludge produced is usually rich in poorly stabilized organic matter, affecting air, water, and soil environment during storage and land spreading. The management of high sludge generated has become one of the challenging tasks for wastewater treatment plants (Neyens and Baeyens 2003). Sludge stabilization is a process to reduce their pathogen content, eliminate offensive odours, and reduce or eliminate organic fraction which induces putrefaction. Technologies commonly used for sludge stabilization are chemical stabilization using lime, thermal stabilization generally by pasteurization and thermal drying, and finally biological stabilization by aerobic digestion, anaerobic digestion, and composting (Chandra et al. 2007).

10.3.1 Anaerobic Digestion

All over the globe, renewable energy technologies are considered as an effective option to reduce fossil fuel dependence and greenhouse gas emissions and to meet rising energy demand. Thus, sustainable waste management has become an elementary building block in a global green economy. Anaerobic digestion process involves the anaerobic reduction of organic matter in the sludge by the action of anaerobic microbe. Anaerobic digestion is generally of two phases: one is hydrolysis and the other is gas production phase (Climent et al. 2007). Digestion process is one of the best stabilizing processes as it can reduce the organic fraction and pathogen and also helps to produce biogas renewable energy (Delgenes et al. 2002). Demirbas (2007) reported that anaerobic digestion is one of the most eco-friendly technologies applied for biological stabilization of solid and liquid wastes. Anaerobic digestion is the process in which organic materials are broken down by a microbial population that lives in an oxygen-free environment. Anaerobic means exactly "without air". When organic substance is disintegrated in an anaerobic environment, the microbes produce a mixture of methane/hydrogen and carbon dioxide gas. Dogruel and Ozgen (2017) stated that anaerobic digestion of domestic, industrial, and agricultural wastewater or organic solid waste produces methane (CH_4) or with control operation produces hydrogen (H_2) gas as a renewable energy. Anaerobic digestion process is selected by many researchers because anaerobic degradation generates only less biomass when compared to aerobic process for sludge stabilization. Nowadays, environmental legislation encourages the digestion process for treating municipal and industrial primary and secondary sludge. The cost of anaerobic treatment of higher organic municipal and industrial waste is less compared to aerobic treatment process. The anaerobic digestion process has four essential stages, namely, hydrolysis, acidogenesis, acetogenesis, and methanogens.

Anaerobic digestion is a technique to stabilize the organic solids in sludge by degrading and reducing the volume of sludge (Lettinga et al. 1999). Anaerobic digestion is the biochemical process that produces high-energy methane/hydrogen gas using organic solid waste as a substrate (Saady and Hung 2015). Li and Fang (2007) reported that anaerobic digestion is the consequence of series of metabolic interactions among various groups of microorganisms. It occurs in four phases: hydrolysis/liquefaction, acidogenesis/fermentation, acetogenesis, and methanogenesis. The first group of microorganism secretes enzymes which hydrolyses polymeric materials to monomers such as glucose and amino acids. These are subsequently converted by second group (*Acetobacter*) to higher volatile facility acids and acetic acid. Acetogenesis is a process in which one group of microorganisms helps to oxidize the intermediate products to acetate, H_2, and CO_2 before they are used by methanogens; the acetogenesis step is crucial for the successful production of biogas. Finally, the third group of bacteria, methanogenic, converts hydrogen (H_2), carbon dioxide (CO_2), and acetate to methane (CH_4). These four steps of AD process are explained in Fig. 10.2.

10.3.2 Hydrolysis

In this step, complex organic polymers are hydrolysed into smaller units such as sugars, long-chain fatty acids, and amino acids. Appels et al. (2008) reported that hydrolysis is performed by different groups of facultative/fermentative bacteria by producing extracellular enzymes. The proteolytic bacteria produce protease that catalyses the hydrolysis of proteins in the organic matter into amino acids; the cellulolytic and xylanolytic bacteria produce cellulases and/or xylanases that degrade cellulose and xylan (both are carbohydrates) in the organic matter to glucose and xylose, respectively; and the lipolytic bacteria produce lipases that degrade lipids in the organic matter to glycerol and long-chain fatty acids. The rate at which hydrolysis takes place is governed by feedstock availability, pH, microbial population, and temperature. Kim et al. (2003) showed that the hydrolysis stage is the major rate-limiting step and lengthens the degradation in anaerobic digestion of waste activated sludge. Some industrial operations overcome this limitation by the use of different pre-treatments to enhance hydrolysis. The applications of pre-treatments to enhance the first step have been found to result in a shorter digestion time and provide a higher biogas/biohydrogen yield (Yadvika et al. 2004).

10.3.3 Acidogenesis

The dissolved sugars, long-chain fatty acids, and amino acids produced by hydrolysis are used in this step either by fermentative bacteria or by anaerobic oxidizers forming acetate and other short-chain fatty acids, alcohols, hydrogen, and carbon

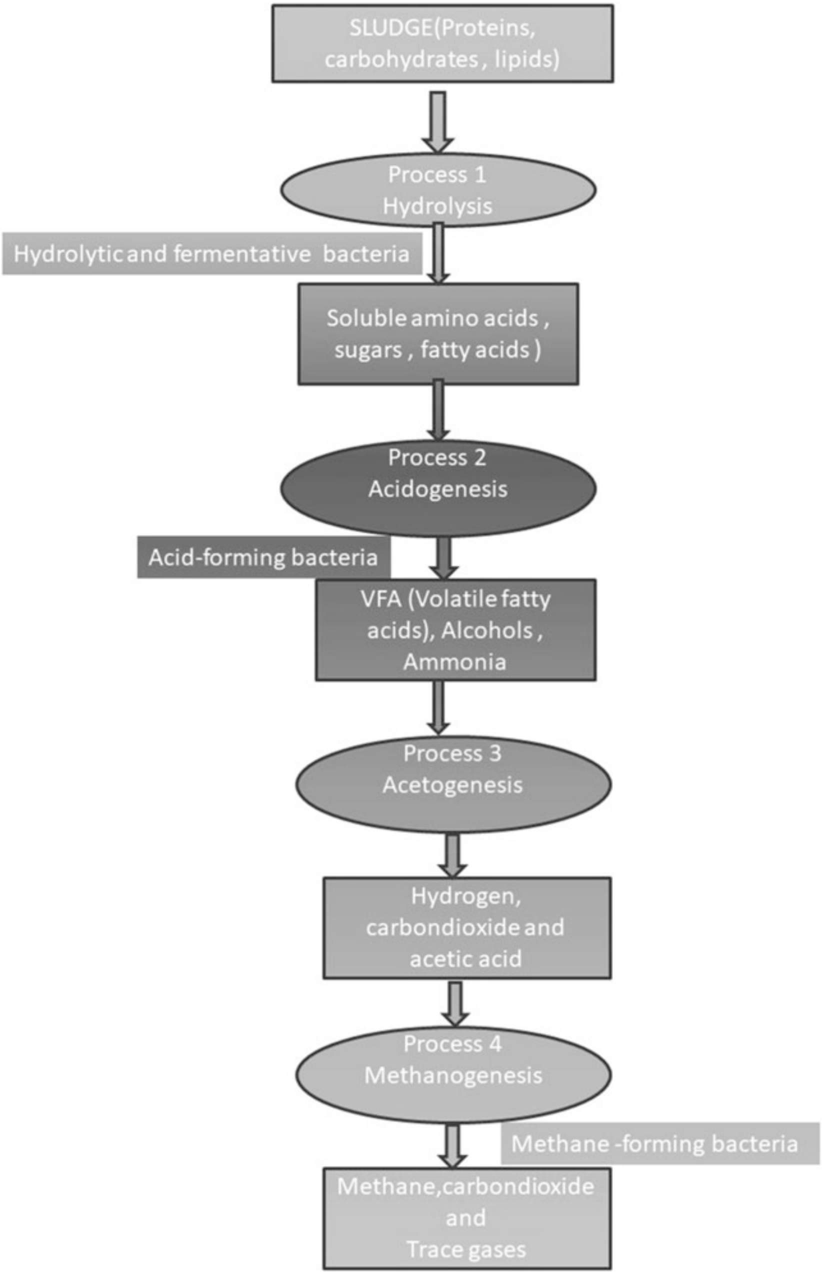


Fig. 10.2 Different stages of anaerobic digestion process of sludge

dioxide. Acidogenesis is a robust and often the fastest step in the whole digestion process. When protons are used as electron acceptor with concurrent hydrogen production, the oxidation of substrate by fermentative bacteria provides the largest amount of energy. Ahring et al. (2002) presented that in a well-operated anaerobic reactor, about 70–80% of the hydrolysis products will be transformed directly to methanogenic substrates, i.e. hydrogen, carbon dioxide, and acetate, with the remaining 20–30% transformed into other intermediate products, such as volatile fatty acids (VFAs) and alcohols. The intermediate products produced in acidogenesis step cannot be utilized by the methanogens and must be further degraded in the acetogenesis step by acetogens.

Under anaerobic conditions, the VFA enters into the acidogenic pathway coupled with H_2 production which is as follows:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2(\text{acetic acid pathway}) \quad (10.1)$$

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O(\text{propionic acid pathway}) \quad (10.2)$$

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2(\text{butyric acid pathway}) \quad (10.3)$$

$$C_6H_{12}O_6 + 2H_2 \rightarrow COOHCH_2CH_2OCOOH + CO_2(\text{malic acid pathway}) \quad (10.4)$$

$$C_6H_{12}O_6 \rightarrow CH_3CH_2OH + CO_2(\text{ethanol pathway}) \quad (10.5)$$

10.3.4 Acetogenesis

Acetogenesis step plays a crucial role in oxidizing acetate, H_2, and CO_2 which can be directly consumed by methanogens to produce biogas (Yadvika et al. 2004). Also, in contrast to the fermentative bacteria, acetogens cannot switch their metabolic pathway but reduce H^+ to H_2. Therefore, the proceeding of acetogenesis is relying on the presence of hydrogen-utilizing methanogens to remove H_2.

10.3.5 Methanogenesis

The final step of the digestion process is called methanogenesis, which mineralizes the fermentative bioproducts into methane. This step is carried out by two main groups of methanogens: the aceticlastic methanogens and hydrogen-utilizing methanogens. Methane is mainly converted from acetic acid by acetoclastic methanogens and hydrogen and CO_2 by hydrogen-utilizing methanogens (Eraqi et al. 2016). Methanogens are pH sensitive; pH should be monitored properly as methanogenesis is the most important process of sludge stabilization. The hydrogen-consuming methanogens are rapid-growing organisms in the digestion process, and the accumulation of hydrogen is more toxic for the microbes. Hydrogen-utilizing methanogenesis is more resistant to environmental changes than acetoclastic methanogenesis which is rate limiting in some cases of anaerobic treatment of easily hydrolysable waste. Tchobanoglous et al. (2003) explained that methanogenesis is used in sewage and other complex wastes treatment as sludge yields are low and it converts the energy of organic matter to energy-rich methane fuel. Feng et al. (2014) reported the methanogenesis reactions can be expressed as follows:

$$CH_3COOH \rightarrow CH_4 + CO_2 \tag{10.6}$$

$$2C_2H_5OH + CO_2 \rightarrow CH_4 + 2CH_3COOH \tag{10.7}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{10.8}$$

Among these, research is being mainly concentrated on hydrolysis and acidogenesis because it produces readily solubilized substances enriched with carbon (Eraqi et al. 2016).

10.4 Advantages of Anaerobic Digestion Process

Anaerobic digestion process is a technology used worldwide for complete depollution, and its advantages are classified in four different classes by Eswari et al. (2016) as follows:

Waste treatment benefits
Organic liquid and solid waste treatment process
Required less land than aerobic composting or landfilling
Produce only lower digested waste thus reducing the disposal waste volume and weight to be landfilled
Tolerant of heavy loadings, actually heavy loadings of 5–10 kg COD/m3 of reactor volume
Environmental benefits
Significantly reduces carbon dioxide and methane emissions
Eliminates odour
Produces a sanitized compost
Transformation of the liquid manure and the manure into a fertilizer, more easily assimilated by the plants, with reduction in the odours and the disease-causing agents
Organic waste processing for competitive prices
Insect elimination at the storage pit
Maximizes recycling and recovery benefits
Helps to achieve zero waste discharge
Potential to treat the sludge in countries considering banning landfilling of waste
Energy benefits
Net energy-producing process
Generates high-quality renewable fuel
Reduces carbon dioxide emissions by displacement of fossil fuels
Biogas (methane or hydrogen) proven in numerous end use applications
Economic benefits
More cost-effective than other treatment options from a life cycle perspective
Additional income
Autonomy in heat in a context of increase in the cost of fossil energies

Diversification of outlets for crops
Reduction of manure purchase thanks to valorization of digested sludge

10.5 Importance of Biological Pre-treatment of Sludge

The maximum amount of soluble substances is produced during the hydrolysis stage of the digestion process, and this soluble substance is subsequently converted to biogas. The rate of hydrolysis is directly proportional to production of biogas produced during the anaerobic digestion process. Among the four stages of anaerobic digestion, the hydrolysis phase is a rate-limiting step (Bougrier et al. 2008) as it involves depolymerization of complex substances. This problem can be overcome by solubilizing the insoluble complex organic matter before entering anaerobic digestion because when the organic matter attains the soluble state. Various mechanical, chemical, thermal, and biological methods are preferred to progress the solubilization of sludge for further utilization or disposal. Tsuyoshi et al. (2010) reported that the biological (microbes/enzyme) methods are favoured due to eco-friendly and low operational cost when compared to other sludge solubilizing methods. Typically, in the biological treatment, the degradation of complex biodegradable organic matters depended on the presence of hydrolytic enzymes (Guo and Xu 2011). Thus, the solubilization of sludge before entering the anaerobic process can enhance the overall anaerobic digestion process by minimizing the retention time of substrate and also increasing the methane/hydrogen production rates. The digestion process produces CH_4 or with control operation produces H_2 gas as a renewable energy.

10.5.1 Biological Pre-treatment

In the biological pre-treatment process, microbial-based hydrolytic enzymes play a vital role in dewatering and reduction of solid content of sludge by reducing the organic compounds and removing the pathogenic organisms and odour (Ayol and Dentel 2005). Thus, the biological process improves the stability of sludge for further utilization or disposal (Roman et al. 2006). Hasegawa et al. (2000) reported that in the biological pre-treatment process, the addition of microbes or complex enzymes or mixture of complex hydrolytic enzymes activates the hydrolysis of organic sludge. Biological treatment is non-economical because researchers use commercialized hydrolytic enzyme for sludge pre-treatment. So, there is a need to find an alternative cheap source of enzymes. There are two ways for biological pre-treatment: cultivating microbe-producing hydrolytic enzymes and extracting crude enzymes from organic solid waste. Many researchers are cultivating hydrolytic enzymes producing microbes from various organic sources for the treatment of WAS (Leal et al. 2006). Merino (2007) reported that microorganisms produce large variety of extracellular enzymes for hydrolysis of organic matter. Kavitha et al. (2014) produced protease and amylase from *Bacillus jerish 03* and *jerish 04* to degrade WAS, and the result concluded that collective effect of protease and amylase helps to enhance sludge solubilization to produce higher amount of biogas through AD process. Merrylin et al. (2012) cultivated *Bacillus licheniformis* from acclimatized sludge, which have the capability to produce protease. This produced protease is used for solubilization of municipal waste activated sludge and yields biogas of 184 mL/g VSS added. Direct addition of microorganisms for stabilization will contribute to a large amount of biomass which increases the sludge volume; instead, it can be reduced by adding an enzyme directly, which is responsible for the degradation (Wawrzyńczyk et al. 2007).

10.5.2 Enzymatic Pre-treatment

A huge number of diverse enzymes (lytic or hydrolytic) have been stated to play a significant role in sludge treatment applications. Watson et al. (2004) reported that hydrolytic enzyme treatment can potentially induce the sludge solubilization and thus minimize the rate-limiting phase in the digestion processes. The solubilization of solids can be by two sets of enzymes: the lytic enzymes resulting in cell wall matrix disruption and the hydrolytic enzymes causing the breakdown of macromolecules (Mayhew et al. 2002). Hong and Herbert (2002) reported that proteins and carbohydrates are the leading components of activated sludge and that their proportions vary according to the characterization of sludge. Thus, biomolecules, proteins, and carbohydrates are the important components of EPS in activated sludge (Houghton et al. 2001). Parmar et al. (2001) stated that the alkaline protease, a hydrolytic enzyme, showed a valuable impact in pathogen reduction and solid reduction and also enhanced dewatering of sewage sludge. They also described that the sewage sludge treatment by an addition of mixed enzymes (alkaline protease along with lipase and cellulase) at 50 °C showed beneficial effects in pathogen reduction. Roman et al. (2006) investigated the combined effect of commercially available enzymes (cellulase and pronase E) in solubilizing the organic municipal waste activated sludge. Yang et al. (2010) demonstrated municipal secondary sludge treatment with hydrolytic enzymes (protease, amylase, and mixed enzyme treatment) and concluded that enzymes can improve the stability of sludge by solid reduction. Lipids are also another important biomolecules present in sludge with higher molecular weights and are also important materials in microorganisms. An extremely high lipid content is present in the wastewater of special industries like oil refineries and restaurants. Therefore, lipid hydrolysis in the sludge using lipase plays an effective role in sludge solubilization (Nagina et al. 2001). Concurrently, lipase has a relevant function in sludge digestion. It can catalyse triacylglycerol and other water-insoluble esters of hydrolysis, esterification, and alcoholysis, as well as transesterification. The increase in soluble COD is a direct measurement of the degradation of suspended matter in the sludge using enzymes. Wawrzynczyk et al. (2003) have shown that enzymatic treatment of sludge from Källby WWTP in Lund with four glycosidic enzymes, one lipase, and one protease increases the release of soluble COD with increasing enzyme dose. The duration of a typical experiment was 4 h, and the temperature was kept at 45 °C with a pH adjustment to 7. TS in the

Table 10.1 Review on hydrolysis of sludge using enzymes

Sludge type	Enzyme	Scale	Effects	Reference
Biological sludge (WWTP)	Mixtures of lipase, glycosidic enzymes	Lab scale	Improved solubilization of organic matter (20–40%)	Wawrzynczyk et al. (2003)
			Reduced vitality	
Primary and waste activated sludge mixture (WWTP)	Mixtures of enzymes	Lab scale	Increased methane production (60%)	Gessesse et al. (2003)
Mixed wastewater sludge	Mixtures of enzymes	Pilot scale, full scale	Increased methane yield (71%)	Wawrzyńczyk et al. (2007)
	Two glycosidic enzymes			
Anaerobically digested sludge (WWTP)	Protease, lipase, and other hydrolytic enzymes	Lab scale	Increase methane production (20%)	Anto et al. (2006)
			Improved dewatering properties	
Primary sewage sludge (WWTP)	Mixture of enzymes (cellulase and pronase E)	Lab scale	Enhanced dewaterability (based on capillary suction hydrolytic enzymes, time, solid content of final product, filtrate turbidity)	Roman et al. (2006)
			Reduction of total solids (80%)	
Sewage sludge	Mixture of enzymes (cellulase and pronase E)	Lab scale	Improved solid reduction and settling of solids	Parmar et al. (2001)

sludge and the enzyme concentration varied, but the ratio between these was kept constant. It was shown that increasing TS content in the sludge released more COD, but the relative release was rather constant. Parawira (2012) reported a review on treatment of various types of WAS using different and mixed enzyme complex as indicated in Table 10.1.

Parawira (2012) also stated the various advantages of enzyme hydrolysis which are as follows:

- Enzymes are cell free, are small and soluble, and are consequently able to reach the substrate easier.
- The enzyme activity can also undergo hydrolysis in the presence of microorganism predators and inhibitors of microbial metabolism.
- They function under a wide range of environmental conditions such as temperature and pH. The enzymes also reduce the volume of the waste, while

microorganisms added contribute to a large amount of biomass which increases the sludge volume.
- Absence of adaptation period as for the microorganisms.
- Easy to control the process.
- Enzymatic hydrolysis is not only energy sparing because of the relatively mild reaction conditions but also avoids the use of toxic and corrosive chemicals.
- Low equipment maintenance.
- The enzymes to be used in hydrolysing complex wastes such as sludge and agricultural residues do not have to be highly purified as was demonstrated for lipid-rich wastes. Such enzyme mixtures may include a variety of enzyme activities capable of numerous catalytic functions for them to be useful in heterogeneous substrates like sludge biomass.
- The major disadvantage of this process is the cost of commercial-based enzymes is too high. Lately, researchers producing hydrolytic enzymes by fermentation process seem to be a good substitute and perform better than costly single enzymes (Wei et al. 2015). Many literatures recommended that if the crude enzyme activity of a biological solution is higher, it can be used directly without any recovery process in a feasible and economical way (Leung et al. 2012). Liu et al. (2013) reported the advantages and disadvantages of various types of pre-treatment process which are very helpful in solubilization of WAS and to increase the bioavailability of biomolecules and which in turn increase the biogas production during anaerobic digestion of pre-treated waste.

10.5.3 Biohydrogen Production from Sludge

Fossil energy source cannot be renewed, and it will be exhausted with progressively more fossil fuel consumptions within the decades. Demirbas (2007) stated that on the basis of sustainable development, biofuels are promising alternatives to renewable energy sources for the future. Biofuels has more advantages over fossil fuels, they are easily biodegradable and help in CO_2 recycling, and its production methodology is eco-friendly in nature (Puppan 2002). On the other hand, the derived biofuels from renewable carbon sources are attractive based on bioresource sustainability, minimized food security, economic feasibility, and land usage issues (Slade et al. 2009). Among biofuels, biohydrogen has received more attention all over the world because it satisfies the basic worldwide environmental protection and sustainable development. Biohydrogen gas is considered as an imperative and versatile biofuel for a sustainable global power supply. Hydrogen gas produced from renewable sources like liquid and solid organic waste using aerobic or anaerobic fermentation process is termed as biohydrogen (Koku et al. 2002). Biological process of biohydrogen-producing microbes acts as a catalyst in an aqueous environmental condition at ambient temperature and pressure. The methods used commonly in the production of biohydrogen from organic solid and liquid waste are photodecomposition (photofermentation) using photosynthetic bacteria, dark fermentation using anaerobic or facultative anaerobic bacteria, and microbial fuel cell (MFC). The competence of hydrogen production by photosynthetic microorganisms is less and will not produce biohydrogen in the absence of light.

Fermentative hydrogen production is more widely used because it has more advantages than photosynthetic microorganism. Fermentative process has simple process control, low operating costs, and high feasibility of industrialization and also has higher hydrogen production stability. Dark fermentation process is more economically feasible as it can use many waste organic substances as feedstock. Extensive research has also been performed in biohydrogen production at high temperature which progresses the reaction kinetics and also augments the assimilation of complex substrates, such as lignocellulosic materials or other waste biomass. Complex solid wastes like wastes from mixed wastes, kitchen, food processing, sludge, and municipal wastes can act as good feedstocks for fermentative hydrogen production. Therefore, countries with large agricultural frugalities have potential for major economic development through producing and using biohydrogen to replace conventional energy sources in various industrial and household activities. Bioreactor design and process parameters are the major governing factors for the production of hydrogen through anaerobic digestion process (Shireen and Das 2008). Nandi and Sengupta (1998) reported that it is necessary to monitor the bacterial growth phenomenon in anaerobic rector to control the production of unstable biohydrogen, which may cause metabolic shift in microbes producing hydrogen. Also, the microbial species involved in the production of hydrogen also need to be taken into account to maximize the biohydrogen production from various biomass. The microbes like *Bacillus*, *Enterobacter*, *Citrobacter*, and *Clostridium* species are involved in the production of biohydrogen from anaerobic dark fermentation process.

Nowadays, many researchers use mixed microbial flora or co-culture methodology for the production of hydrogen from various organic waste sources other than pure cultures. From the engineering point of view, the selection of mixed cultures is considered to be favourable for a full-scale application because no medium sterilization is required, which makes the process control operation easier, reduces the overall process cost, and also made researchers select extensive feedstock for production of biohydrogen (Valdez et al. 2005). It also observed that a pure microorganism has fewer hydrolytic activities needed to degrade complex wastes, when compared to mixed cultures. Thus, producing mixed microbial consortium becomes a thrust area for researchers.

The anaerobic digestion helps in extracting renewable energy from domestic, industrial, and agricultural liquid and solid organic waste to produce methane (CH_4) or with slight operation control process as hydrogen (H_2). H_2 is preferred over CH_4 because it has more calorific energy per unit mass when compared to CH_4 and CO_2 gas not generated when combusting hydrogen gas; thus, hydrogen gas helps in carbon sequestering at the production site. Hallenbeck (2005) reported that biohydrogen production from renewable sources by fermentation process made them the best and promising alternative bioenergy. Saratale et al. (2008) reported that biohydrogen helps to address the issue of many rural sectors in the globe, like energy security and environmental and social economic problems. Sustainable

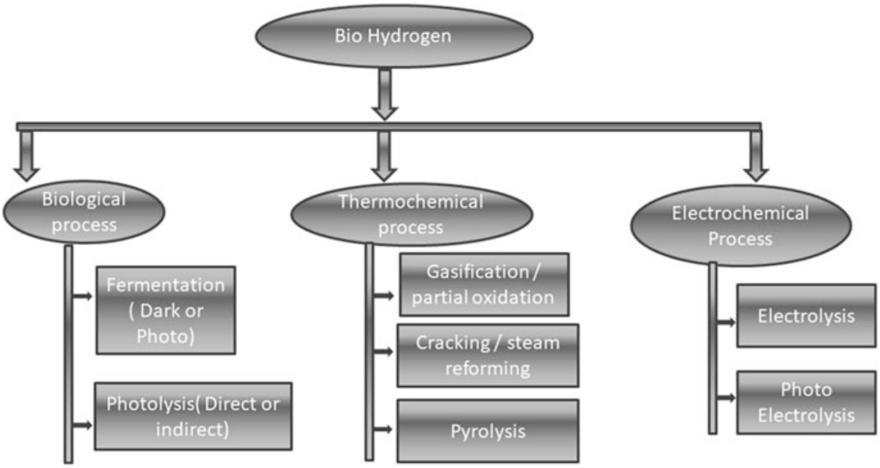


Fig. 10.3 Biohydrogen production methods

Table 10.2 Different pathways of biohydrogen production

Process	Pathway
Biophotolysis H_2 production by green algae and cyanobacteria (Water splitting)	$12H_2O + \text{“light energy”} \rightarrow 12H_2 + 6O_2$
Photoproduction of H_2 by phototrophic bacteria	$C_2H_4O_2 + 2H_2O + \text{“light energy”} \rightarrow 2CO_2 + 4H_2$
Fermentative H_2 production by fermentative bacteria	$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$
	$C_6H_{12}O_6 + 2H_2O \rightarrow CH_2CH_2CH_2COOH + 2H_2 + 2CO_2$
Combined system using photosynthetic and fermentative bacteria	$C_6H_{12}O_6 + 2H_2O \rightarrow 2\ C_2H_4O_2 + 2CO_2 + 4H_2$
	⬇
	$C_2H_4O_2 + 2H_2O + \text{“light energy”} \rightarrow 2CO_2 + 4H_2$

production of Bio-H_2 required the substrate, culture, and any other material used for production should be taken from renewable and sustainable sources. In general, Bio-H_2 can be produced using different methods like biological, thermochemical, and electrochemical processes as indicated in Fig. 10.3.

The methods used commonly in the production of biohydrogen from organic solid and liquid waste are photodecomposition (photofermentation) using photosynthetic bacteria, dark fermentation using anaerobic or facultative anaerobic bacteria, and combination of both as indicated in Table 10.2 (Valdez et al. 2005).

Among them, dark and photofermentation process is preferred as it can utilize renewable feedstock for bio-H_2 production and also the effluent from them can be recycled to produce value-added products. Levin et al. (2004) reported that dark anaerobic fermentation has the superlative potential for real-world production of bio-H_2 from renewable organic waste materials than photofermentation process. The lower energy requirement, speed of bio-H_2 production, simple technical process

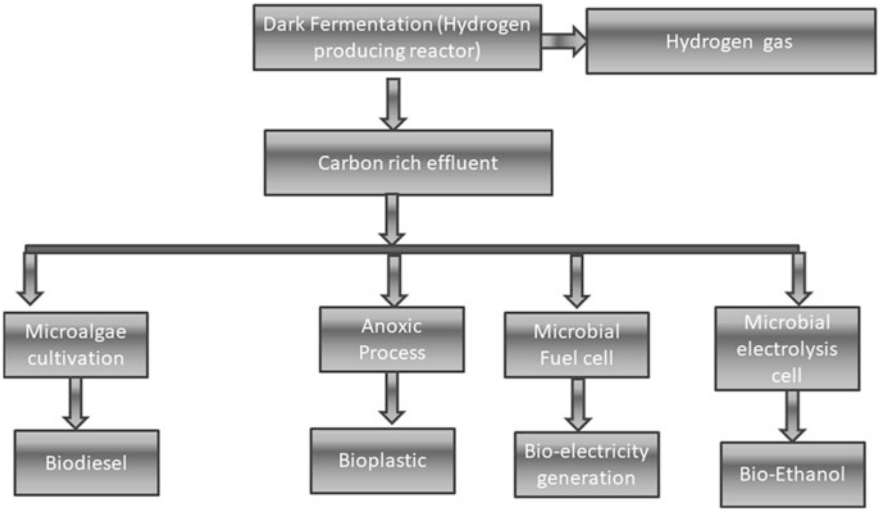


Fig. 10.4 Uses of liquid effluent from hydrogen reactor

which can utilize high carbon content organic waste or refuse, and economic viability are the major advantages of hydrogen produced from dark fermentation process. This type of process also produces hydrogen without using any light sources and also helps to produce other useful value-added products like VFA (volatile fatty acids) and alcohols as a by-product (Fig. 10.4). Nandi and Sengupta (1998) reported that this type of dark fermentation process occurs in the absence of O_2 and thus this process helps to overcome O_2 limitation process.

Kapdan and Kargi (2006) stated that the bacteria like *Clostridium* sp., facultative anaerobes (*Enterobacter* and *Bacillus* sp.), and bacterial consortium (anaerobic digester sludge, soil, and animal faeces) are common microorganisms involved in the production of bio-H_2. Chandrasekhar et al. (2015) stated that the dark fermentation of solid organic waste will result in biohydrogen as the main product and liquid effluent as a by-product, which is in turn used to produce biodiesel, bioplastic, bioethanol, and bioelectricity (Fig. 10.4).

10.6 Factors Influencing Biohydrogen Production by Dark Fermentation

10.6.1 Substrate for Dark Fermentation

Dong et al. (2009) reported the various renewable biomass utilized by the dark fermentation process for the production of biohydrogen are forest residues, crop residues, agricultural waste, waste from processing of agricultural products, livestock residues, energy crops, algae biomass, wood waste, food processing, and industrial (dairy wastes, oil mill waste, glycerol waste, etc.) and municipal organic solid waste. Biotransformation of organic liquid and solid waste to biohydrogen is a more significant process when considering environmental pollution control and economic factors like resource recovery and low total cost waste management. Sewage WAS has enormous amounts of carbohydrates, lipids, proteins, and other minor nutrients, which could be exploited for anaerobic biohydrogen production (Hallaji et al. 2019). Yang et al. (2012) reported that sewage sludge can be used for the production of biohydrogen along with solubilization of WAS using in situ ultrasound pre-treatment. Wang et al. (2003a) reported that the hydrogen yields of 1.2 mg H_2/g Che and 0.6 mol/kg COD, respectively, were obtained when waste activated sludge used as the raw material. Lay (2001) reported that heat pre-treatment of digested sludge increases biohydrogen production potential. Wang et al. (2003b) presented the pre-treated sludge increased the soluble COD, thus improving the hydrogen yield (0.9 mmol/g dried sludge).

10.6.2 Mixed Cultures for Biohydrogen Production

Microorganisms also play an important role in large-scale production of biohydrogen process. According to the biochemical engineering point of view, the mixed microbial consortium is more favourable for large-scale product of biohydrogen when compared to using pure microorganisms. Valdez et al. (2005) stated that by using microbial consortium, one can reduce the complex process control operation, no sterilization is required, it helps in reducing the overall cost, and it can use the broad range of feedstock. Mshandete et al. (2008) reported that microbes produce hydrolytic enzymes like amylase, protease, cellulase, and lipase to solubilize complex biomolecules into simple sugars, glycerol, and fatty acids, which can be easily utilized by microbes to produce biohydrogen. In general, single microorganisms can produce less hydrolytic enzymes, which act on complex organic waste to solubilize them for biohydrogen production. The degradation of renewable organic matter in anaerobic fermentation by microbial consortia helps to produce a stable and self-regulating fermentation for biohydrogen production. Noike and Mizuno (2000) produced mixed microbial consortium from sewage sludge for the production of biohydrogen. Koutrouli et al. (2006) reported that mixed microbial consortium is produced using anaerobically digested sludge, acclimated sludge, compost, soil, land, and animal manure, respectively. The conventional microorganisms found in certain waste (waste starch and cellulose containing agricultural wastes, food industry wastes, carbohydrate-rich industrial wastewater, and organic wastewater) can be useful for direct utilization and solubilization of organic-rich substances for the production of biohydrogen.

10.6.3 Hydraulic Retention Time (HRT)

The organic loading rate of the wastewater impacts the hydrogen production pattern, apart from other wastewater characteristics. Addition of sewage sludge to the anaerobic reactor increases the biohydrogen production process since it contains micronutrients, organic matter, and microbial biomass. The effect of HRT (48 to 8 h) on hydrogen production from brewery solid waste by cattle dung compost at pH 5.5 was investigated. Fan et al. (2006) showed the maximum hydrogen production at 18 h HRT and suggested that hydrogen yield is reduced with increases in HRT. It is also reported that the biomass activity also depends on HRT. With each gram of biomass producing 65–145 mmol H_2/day, it is important to optimize HRT to achieve maximum hydrogen production. The glucose feeding rate is lower, and H_2 yields become higher and vice versa as observed by Fang and Liu (2004). Thus, HRT is also one of the most significant factors to increase the production of biohydrogen.

10.6.4 pH

Chen et al. (2001) reported the maximum specific hydrogen production when maintaining the pH range at 5–6. Some other researchers showed that pH 6.8–8 has the capability to produce maximum hydrogen gas (Khanal et al. 2004). This confirms that the acidic pH is favourable for improving the production of biohydrogen. The optimal range of pH for biohydrogen production for various substrates using dark fermentation process is presented in Table 10.3. Hence, the most important parameter is obtaining the first initial value of pH and managing the value over the period of production.

Table 10.3 Optimum operating pH for dark fermentation processes

Optimal pH	Organism	Substrate	Hydrogen yield	Reference
5.5	Mixed culture	Glucose	2.1 mol H_2/mol glucose	Fang and Liu (2004)
5.5	Mixed culture	Glucose	1.9 mol H_2/mol glucose	Zhang et al. (2006)
5.5	*Clostridium* sp.	Sucrose	89.8 mL/g sucrose	Fan et al. (2004)
5.5–5.7	Mixed culture	Sucrose	214 mL/g COD	Khanal et al. (2004)
5.5	Mixed culture	Brewery mixture	43 mL/g COD	Fan et al. (2006)
5.5–5.7	Mixed culture	Starch	125 mL/g COD	Khanal et al. (2004)
5.5	Mixed culture	Sucrose	234 mL/g COD	Chen et al. (2006)
5.5	Mixed culture	Non-fat dry milk	119 mL/g COD	Chen et al. (2006)
5.5	Mixed culture	Food waste	101 mL/g COD	Chen et al. (2006)
6.0	*C. saccharoperbutylacetonicum*	Cheese whey	7.89 mmol/g lactose	Ferchichi et al. (2005)

10.6.5 Temperature

Bailey and Ollis (1986) stated that temperature is also a significant environmental factor prompting the growth rate and metabolic activities of hydrogen-producing bacteria. Generally, fermentation of organic matter for biohydrogen production was conducted under mesophilic (30–45 °C) or thermophilic condition (50–60 °C) (Valdez et al. 2005). Optimal temperature for H_2 production by dark fermentation mainly depends on the type of microorganisms and substrates used. Yu et al. (2002) studied the effect of temperature (20–55 °C) on hydrogen production from rice winery wastewater by mixed anaerobic cultures in an upflow anaerobic reactor and suggested 45 °C gives a maximum yield. The optimal range of temperature for biohydrogen production for various substrates is presented in Table 10.4.

10.7 Co-digestion

Co-digestion is process in which two or more substrates undergo instantaneous anaerobic digestion. Co-digestion of sludge with organic fraction of solid waste, in anaerobic reactors, is the best available option for the treatment and disposal of solid organic waste. Co-digestion process is an easier process to manage mixed solid wastes from municipal treatment plants (Lin et al. 2011). Some other researchers reported that it is better to avoid addition of extract nutrients to digester in order to improve the performance (Neves et al. 2009).

Factors that influence the anaerobic co-digestion process are as follows:

Table 10.4 Optimum operating temperature for dark fermentation processes

Optimal temperature (°C)	Organism	Substrate	Hydrogen yield	Reference
35	Mixed culture	Sucrose	234 mL/g COD	Chen et al. (2006)
35	Mixed culture	Non-fat dry milk	119 mL/g COD	Chen et al. (2006)
35	Mixed culture	Food waste	101 mL/g COD	Chen et al. (2006)
37	Mixed culture	Sucrose	214 mL/g COD	Khanal et al. (2004)
37	Mixed culture	Starch	125 mL/g COD	Khanal et al. (2004)
37	Mixed culture	Brewery mixture	43 mL/g COD	Fan et al. (2006)
41	Mixed culture	Glucose	1.67 mol-H_2/mol-glucose	Mu et al. (2006)
55	*Thermoanaerobacterium*	Starch	92 mL/g starch	Zhang et al. (2003)

- Mixing ratio of substrate and co-substrates
- Macro- and micronutrients
- C/N ratio
- pH
- Presence of inhibiting substances
- Presence of readily biodegradable organic matter
- Alkalinity
- Temperature
- Hydraulic retention time (HRT)
- Solids loading rate (SLR)

Murto et al. (2004) examined anaerobic co-digestion processes with the organic waste like sewage sludge, industrial waste, slaughter house waste, fruit and vegetable waste, manure, and agricultural biomass, and the result confirmed the co-digestion process enhances production of biogas. The co-digestion of primary sludge and the organic fraction of municipal solid waste at different mixing conditions in digesters with organic loading rate of 2.5–3.6 g VS/day for primary sludge and 2.5–4.3 g VS/day for primary sludge with municipal solid waste were performed under mesophilic conditions. The result showed that the absence of agitation resulted in the reduction of specific gas production (SGP) and suggested that appropriate contact between the substrate and the microbes was required (Gomez et al. 2006). The result showed the increase in biodegradability of 87% and 43% for primary and secondary sludge, respectively, and the biomass in secondary sludge decomposed much faster than the biomass in primary sludge. Viotti et al. (2004) reported that it is required to form a homogeneous mixture of organic wastes with sludge in a ratio of 2:5 to enhance the performance of anaerobic digestion process.

10.8 Biohydrogen Applications

Mohammed et al. (2011) reported various applications of biohydrogen are as follows:

- Petroleum and chemical industries, like fossil fuel processing, ammonia manufacturing, and petrochemicals (hydrodealkylation, hydrodesulphurization, and hydrocracking)
- Hydrogenation agent to increase the level of saturated fats and oil
- Hydrodeoxygenation for oxygen removal and saturation of double carbon bonds
- Hydrotreatment/upgrading of bio-oils to transportation fuels
- Metal production and fabrication
- Electronic industry
- Transportation sector
- Energy storage technology

- Pharmaceuticals
- Fuel for rocket propulsion

10.9 Biopolyester (PHA)

PHA is a biopolyester produced by a consortium of microbial sources through fermentation when an essential nutrient is inadequate. Generally, biopolyester termed as green bioplastic is an alternative to traditional polyester as it shows biodegradable and biocompatible properties. It can be applicable for coating and packing of materials, but it has noteworthy application in medicinal fields like preparation of medical utensils (surgical sutures) and acts as biodegradable carriers in drug delivery control systems and treatment of fibrous ligaments and cartilage tissues (Pereira et al. 2013). Many researchers have reported that microbial strains are the rich source for biopolyester production under an optimized fermentation process. Bhuwal et al. (2013) discussed that 42 bacterial strains were used to produce biopolyester at 37 °C for 3 days in batch fermentation process. Sodium hypochlorite (NaClO) was used as a biopolyester extraction solvent. Among the bacterial strains, *Enterococcus* and *Brevundimonas* species produced 5.2 g/L and 4 g/L of biopolyester, respectively. The list of various microbial strains and sources that were used for biopolyester production is depicted in Table 10.5.

Lopez et al. (2018) stated that the commercial biopolyester or microbial-based biopolyester is too expensive as substrate selection (carbon/nitrogen source), identification, and culturing of bacterial strain under sterile condition, recovery, and purification of biopolyester. These cost restraints can be resolved by using sludge as a source for biopolyester extraction because 40% of biopolyester (dry cell weight basis) is ensued in sludge as reported by Takabatake et al. (2002). Biopolyester extraction solvents such as trichloromethane, methylene chloride, chloropropane, sodium dodecyl sulphate (SDS), and NaClO were used to extract biopolyester from microbial, plant, and sludge sources. Subsequently, the extracted biopolyester was decolorized with activated carbon or ozone (Anjum et al. 2016).

Table 10.5 Various microbial strains and sources used for biopolyester production

Biopolyester	Microbial strain	Sources	References
PHAs	*P. fluorescens* A2a5	Sugarcane liquor monosodium glutamate	Chen and Jiang (2017)
mcl-PHAs[a]	*P. aeruginosa* ATCC 27853	Carinata oil	Impallomeni et al. (2018)
PHAs	*Pseudomonas* strain-P(16)	Soy molasses and date molasses	Aljuraifani et al. (2019)
PHAs	*C. necator* DSM 545	Waste glycerol	Mathuriya and Yakhmi (2019)
PHAs	*T. thermophilus* HB8	Lactose from whey-based media	Chen and Jiang (2017)

[a] *mcl-PHAs* medium-chain-length PHAs

Sethupathy and Sivashanmugam (2018) investigated the influence of coupled chemicals (NaClO-chloroform ($CHCl_3$)) on hydrolytic enzymes extracted from sludge using sonic wave combined rhamnolipid for biopolyester extraction. The extraction time (2 h) was enough to attain a higher biopolyester release and reported to be 0.87 g/g with the limited dose of NaClO-$CHCl_3$ (30% v/v). Also, the obtained the biopolyester was decoloured with activated carbon to attain white-coloured biopolyester. Sethupathy and Sivashanmugam (2021) carried out the batch study to boost up the recovery of biopolyester from waste sludge. During their study, municipal aerated waste sludge (MARWS) was chosen as a substrate and attained a maximal biopolymer extraction (910 mg/g) with respect to 1 h of recovery time and 4000 μL of dimethyl carbonate dose. The results confirmed that the waste biomass aids to extract more biopolyester without prior treatment by using green solvents when compared to microbes as a source for biopolyester recovery.

10.10 Conclusion

Strict environmental laws on an Industrial effluent disposal, making the industries adopt extensive treatment before being discharged into the natural water bodies. Biological treatment processes offer a cost-effective method to remove organic compounds and nitrogen from dairy wastewater. In municipal wastewater treatment and industrial effluent treatment plants, aerobic biological treatment (activated sludge process) process plays an important role in reducing the organic matter and producing excess sludge which in turn needs to be treated further before disposal. Ineffective and inappropriate solid waste management (SWM) is responsible for numerous problems such as low-level sanitation, higher odour generation, environmental (soil and ground/surface water) pollution, etc. Therefore, many researchers are working to develop cost-effective, recyclable, or reusable technologies to utilize sludge effectively. AD process is one of the best-stabilizing processes as it can reduce the organic fraction and pathogen and also helps to produce biogas renewable energy. Globally, the interest in biochemical products (organic acids, enzymes, biopolymers (PHA), etc.) production from organic waste and sludge is increasing day by day. Also, fossil energy sources cannot be regenerated and will be exhausted with increasing usage within decades. Biofuels are promising alternatives to renewable energy sources for the future. Among biofuels, biohydrogen made from organic solid waste (sludge) has received more attention all over the world because it satisfies the basic worldwide environmental protection and sustainable development.

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Microwave-Assisted Chemically Modified Biochar for the Sequestration of Emerging Contaminants

11

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Abstract

The use of biochar produced from waste biomass is growing in popularity for addressing the most important ecological issues. Biochar is a carbon-rich by-product produced through the pyrolysis or carbonization of plant and animal biomass. Biochar (BC) shows great potential as an adsorbent in decontaminating waters. The question of the beneficial application of biochar has raised multidisciplinary research concerns in both science and engineering. Feedstock composition and type and pyrolysis conditions, such as temperature and time, significantly influence the properties of pyrolyzed biochar. Another particular application for biochar is activating its properties so as to eliminate specific contaminants. A microwave-based heating method is an alternative healing method that has been successfully used in biomass pyrolysis for biochar because of its rapid, volumetric, selective, and efficient heating. Biochar production from a wide variety of

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biomass sources, factors affecting its properties, biochar utilization for organic and inorganic contaminants remediation, and microwave-assisted pyrolysis (MWP) of biomass are discussed here. Along with this, the study focuses on the characteristics of biochar derived from MWP, microwave absorbers (MWAs), and catalysts applied to MWP, in addition to comparisons of biochar derived from MWP and conventional pyrolysis (CP).

Keywords

Biochar · Production techniques · Modification methods · MWP · Inorganic and organic pollutants removal

11.1 Introduction

11.1.1 Biomass as a Feedstock

Biomass resource was the first and is currently the third largest global source of energy, comprising up to 40–50% of energy usage in many developing countries that have large agriculture and forest areas (Domínguez et al. 2006; El-Naggar et al. 2019a, b). A variety of energy needs can be met with biomass, including power generation, home heating, and industrial process heating. Any living matter can be used as biomass. In more detail, biomass is a material obtained from plants or animal manure that is primarily compounds of carbon, hydrogen, oxygen, nitrogen, and smaller amounts of other elements. According to a typical analysis of dry wood yields, Carbon constitutes 52.42%, Hydrogen: 6.35%, Oxygen 40.83%, and Nitrogen 0.4%. By converting sunlight into plant material, green plants produce biomass (El-Naggar et al. 2019a, b; Abbasi and Abbasi 2010). Photosynthesis, which is a naturally occurring process, is powered by solar energy stored in the chemical bonds of biomass. When biomass is burned, this energy is released as heat. For that reason, biomass species are considered renewable sources of energy that do not add carbon dioxide to the environment, in contrast to non-renewable fossil fuels. In addition, the unique feature of biomass is that it is the only renewable energy source that can produce convenient solid, liquid, and gaseous fuels (Tables 11.1 and 11.2). Pyrolysis temperature and time (slow or fast) strongly influence the yield of biochar. Feedstocks for the production of biochar, such as plant biomasses, are primarily comprised of cellulose, lignin, and hemicellulose (Rutherford et al. 2012). As the temperature enhances, these constituents are gradually pyrolyzed. Compared to cellulose and hemicellulose, lignin is much more recalcitrant during the process of pyrolysis. Production of biochar from biomass, such as wood, involves a pyrolysis process which could be differentiated by residence time (e.g., slow and fast pyrolysis process), temperature, feedstock size, pressure, and heating rate. Feedstock selection can also be regulated to manipulate the physicochemical characteristics of biochar. By using the Institute of Gas Technology (IGT) formula, the high heating value

Table 11.1 Lignin, cellulose, and hemicellulose content of agricultural biomass (Ahmad et al. 2012; Dehkhoda et al. 2010; Gollakota et al. 2017; Bridgwater 2012; Azargohar and Dalai 2008; Zhang et al. 2015)

Feedstock	Lignin (%)	Cellulose (%)	Hemicelluloses (%)
Wood	25–30	35–50	20–30
Wheat straw	15–20	33–40	20–25
Switchgrass	5–20	30–50	10–40
Sugarcane bagasse	23–32	19–24	32–48
Miscanthus	17	24	44
Corn stover	16–21	28	35
Olive husk	48.4	24	23.6
Corncob	15	50.0	31
Tea waste	40	30.20	19.9
Walnut shell	52.3	25.6	22.7
Almond shell	20.4	50.7	28.9
Sunflower shell	17	48.4	34.6
Nutshell	30–40	25–30	25–30
Paper	0–15	85–99	0
Rice straw	18	32.1	24
Leaves	0	15–20	80–85

(HHV) of raw biomass and pyrolysis products is calculated in Eq. (11.1) (Ahmad et al. 2012c).

$$\mathrm{HHV} = 0.36\,\mathrm{C} + 1.38\,\mathrm{H} - 0.016\,\mathrm{Ash} - 0.13\,(\mathrm{O} + \mathrm{N}) + 0.07 \tag{11.1}$$

11.1.2 Biochar Definition

Biochar is a newly constructed scientific term. According to Lehmann and Joseph (2009), it is defined as a carbon-rich product that results from heating biomass, such as wood, manure, or leaves, in a closed vessel without much or no air. Shackley et al. (2012) defined biochar more descriptively as "the porous carbonaceous solid developed by the fast pyrolysis transformation of biomass composites in an oxygen-depleted atmosphere, with physicochemical properties suitable for protracted sequestering carbon in the environment." Verheijen et al. (2010) also defined biochar as "biomass that has been pyrolyzed in a zero or low oxygen environment applied to the soil at a specific under current and future management, a site that is predicted to sustainably absorb carbon and improve soil functions while avoiding short- and long-term negative consequences on the wider environment, as well as human and animal health."

The global energy requirement is currently increasing owing to the increase in population. All sectors in the country require energy (Cao and Harris 2010; Brewer

Table 11.2 Physicochemical properties of selected biomass feedstock (Zhang et al. 2015)

Physical characteristics of some selected biomass materials

Feedstock	Density (kg/m^3)	Moisture content (%)	Ash content (%)	Volatile matter (%)	Fixed carbon (%)
Wood	1186	20	0.4–1	82	17
Bituminous coal	–	11	8–11	35	45
Hybrid polar	150	45	0.5–2	–	–
Switch grass	108	13–15	4.5–5.8	–	–
Barley strew	210	30	6	46	18
Sugarcane bagasse	1198	–	3.2–5.4	–	–
Wheat straw	1233	16	4	59	21
Rice straw	200	6	4.3	79	10.7
Firewood	–	7.74	1.98	80.86	17.16
Birch	125	18.9	0.004	–	20
Pine	124	17	0.03	–	16
Polar	120	16.8	0.007	–	–

Chemical characteristics of some selected biomass materials (Wang et al. 2006)

Feedstock	Carbon (%)	Hydrogen (%)	Oxygen (%)	Nitrogen (%)	Ash (%)
Wood	51.6	6.3	41.5	0.1	1
Bituminous coal	73.1	5.5	8.7	1.4	9
Switch grass	44.77	5.79	49.13	0.31	4.30
Barley strew	45.7	6.1	38.3	0.4	6
Wheat straw	48.5	5.5	3.9	0.3	4
Birch	44	6.9	49	0.1	0.004
Pine	45.7	7	47	0.1	0.03
Polar	48.1	5.30	46.10	0.14	0.007

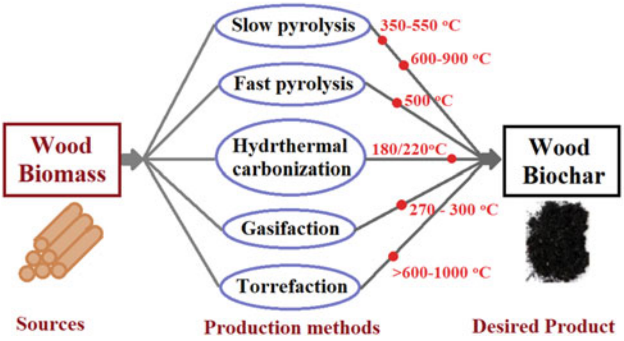
et al. 2014; Chen et al. 2011a). Fossil fuels are the main source of energy. But owing to the effect of CO_2 on the environment and global energy issues, the replacement of fossil fuels has become necessary (Chen et al. 2019, 2011b, 2014a, b). Organic waste, as the main ingredient of solid biomass, has a high potential for biochar generation (Chia et al. 2015; Wei et al. 2017; Czernik and Bridgwater 2004). Biomass waste materials appropriate for biochar production include crop residues from agriculture, forestry, municipal solid waste, food and animal manures, etc. (Houben et al. 2012; Debalina et al. 2017; Demirbas 1997). The biochar derived from biomass is a highly rich source of carbon produced from biomass using thermal combustion in an oxygen-limited environment (Demirbas 2004a, b). The unique properties of biochar, such as large surface area, high porosity, functional groups, high cation exchange capacity, and stability, make it suitable for various applications. The fast and ease of preparation, eco-friendly nature, reusability, and cost-effectiveness are a few advantages of biochar (El-Hendawy 2003; Yargicoglu et al. 2015). Biochar has gained the attention of many researchers in establishing its efficiency in the removal of various contaminants.

11.1.2.1 Production of Biochar Using Thermochemical Processes

Gwenzi et al. (2017) reported thermochemical processes for the production of biochars, including wood-based biochar, which involve conventional/slow pyrolysis, fast pyrolysis, gasification, torrefaction, and hydrothermal conversion. These technologies are categorized mainly based on temperature and residence time during the biochar production processes (Garlapalli et al. 2016; Goyal et al. 2008). Various processes for the production of biochars, including wood-based biochar, are presented in Fig. 11.1. In the following sections, the most important technologies for wood biochar production currently in use are briefly reviewed.

Slow and Fast Pyrolysis

Based on the differences in rate of heating, pyrolysis can be classified into slow and fast pyrolysis. Fast pyrolysis involves heating the biomaterial (pyrolysis) at a faster rate (typically >300 °C/min) for a short residence time (typically less than 60 min) in the absence of oxygen. This process generally yields syngas (low-energy-density gas), bio-oil (high-energy-density liquid), and biochar. In general, a very high yield of 50–70% bio-oil and low yields of 10–30% biochar and 15–20% syngas can be achieved through fast pyrolysis. On the other hand, slow pyrolysis involves heating the biomaterial (pyrolysis) over a varied temperature range (300–800 °C) at a slower rate (typically >5–7 °C/min) for a prolonged residence time (typically greater than 60 min) in the absence of oxygen. This process generally produces more biochar than fast pyrolysis. Pyrolysis is a less cost and robust technology, which can result in the thermochemical decomposition of organic matter into non-condensable syngas, condensable bio-oil, and a solid residual co-product, biochar. Optimized and advanced pyrolysis systems have been used recently to control biochar quality (Haeldermans et al. 2019). It has been well established that biochar, including



180/220 °C

wet/dry biomass

Fig. 11.1 Wood biochar production from wood biomass wood biochar, can be produced through thermochemical decomposition and cracking of organic material at elevated temperatures (250–850 °C) (Hale et al. 2011).

Torrefaction

Torrefaction is a thermochemical treatment process that is carried out under atmospheric pressure, and operating temperature ranging from 200 to 300 °C under limited or no O_2 supply, with low heating rate (<50 °C/min) and long residence time up to 1 h (Hansen et al. 2015; Igalavithana et al. 2017a, b). The end component is a constant substance rich in carbon, which is called torrefied biomass—biochar and biocarbon. Torrefaction products (biochar and biocarbon) can be characterized by specific properties. Biochar has a high energy density and contains 80–90% of potential energy while lessening its mass to 70–80%; thereby, energy density can indeed be increased by 30%. This process can help improve the physicochemical properties of feedstock and aid in the production of biofuel from biomass. The solid products obtained from torrefaction have some advantages such as (1) high energy density and heating value, (2) reduced transport cost due to reduced moisture of the end product, (3) high resistivity of torrefied biomass to fungal attack given its hydrophobic nature, (4) reducing grinding energy requirements, and (5) creating a uniform fuel for gasification or co-firing for electricity (Igalavithana et al. 2017a, b).

Gasification

Thermal carbonization of diverse biomass residues is a viable technology for incorporating bioenergy growth and biochar production (Inyang et al. 2016). Gasification biochar generally contains a considerable amount of minerals and recalcitrant carbon (IPCC 2013; Lehmann 2009; Menendez et al. 2010). The gasification process is undertaken at much higher temperatures than pyrolysis and torrefaction (Kastner et al. 2012). During this process, the energy in wood biomass or any other organic matter could be converted to combustible gases at temperatures ranging from 600 to 1000 °C, producing biochar, water, and condensable tar as minor products (Menendez et al. 2010). The biochar produced as a result of slow pyrolysis possesses a greater aromatic nature than that obtained by the fast pyrolysis process or gasification (Brewer et al. 2009). For this reason, most studies have focused on preparation of biochar using slow pyrolysis and hydrothermal carbonization technology which could yield higher surface area and surface functional groups responsible for sequestering potentially toxic elements (PTEs) onto biochar biomass.

Hydrothermal Carbonization (HTC)

Hydrothermal carbonization is an efficient method to produce biochar from biomass. In comparison to slow pyrolysis, hydrothermal carbonization (at 220 °C, 2.2 MPa) yields biochar with a higher amount of carbon. Biochar produced by the hydrothermal carbonization process is enriched with O-containing functional groups and surface charge, and it is more acidic than biochar obtained through slow pyrolysis. However, relatively higher energy is consumed in hydrothermal carbonization because it requires biomass with high moisture content (Qian and Kumar 2015; Kan et al. 2016). The hydrothermal carbonization process includes several reaction mechanisms, such as hydrolysis, dehydration, decarboxylation, polymerization, and aromatization, although the detailed reactions have been only well characterized for a few types of biomass, such as cellulose. The process takes place effectively only in water and is exothermic. The products of the HTC are a solid phase or "HTC coal" and a liquid phase, referred as process water. A small amount of gas is also produced.

11.1.2.2 Physical and Chemical Characterization of Wood Biochar

Cellulose, hemicellulose, lignin, and extractives in selected groups of woody biomass in comparison with other feedstock are provided in Kan et al. (2016). Here, the major physical and chemical properties of wood-based biochar are summarized in Table 11.3.

Surface Area

The surface area of wood biochar is a crucially important physical property because it can affect the efficiency of biochar to remove PTEs in water. The biochar surface area is a function of biochar production feedstock and operating conditions, principally with the production temperature (Kim et al. 2019). BET is a method commonly used to calculate the biochar surface area by measuring the amount of liquid N_2 adsorption on the biochar surface at a low temperature (77 K). The CO_2 adsorption method at a relatively high temperature (273 K) has also been used to calculate the biochar surface area and shown to be more sensitive and provide more accurate biochar surface area measurements. The surface area of wood biochar is much affected by the pyrolysis temperature, as mentioned in the section "Slow and Fast Pyrolysis." Zama et al. (2017) produced mulberry (*Morus alba*) wood biochar by increasing temperatures from 350 to 550 °C, which resulted in increased surface area of biochar from 16.5 to 58.0 m^2/g. Figure 11.1 shows methods for the production of biochar from wood biomass where two different temperatures prevail for hydrothermal carbonization representing wet or dry biomass.

Chemical Characterization

Elemental Composition and pH

Elemental composition in wood biochar could be used to predict its hydrophobicity, carbonization, and polarity. The H/C molar ratio has been used to estimate the degree of carbonization of wood biochar. The lower H/C molar ratio indicates a higher degree of carbonization and lower amounts of original plant organic residues (e.g., cellulose, hemicellulose), which is observed in high-temperature biochar and vice versa (Luo et al. 2019). The O/C molar ratio has been used to denote the hydrophilic nature of biochar, and as such, it could depict the polar group contents in wood biochar derived from carbohydrates in biomass.

The pH of wood-based biochar differs widely (4.6–11.4) based on the source of feedstock. In addition, pyrolysis temperature is a critical factor affecting the pH of wood biochar. For example, the pH of oak wood biochar produced at 200 °C is lower ($pH = 4.60$), but at 400 and 600 °C, the biochar was neutral to alkaline pH (6.9–9.5). Increasing biochar pH with increasing pyrolysis temperature might be attributed to

Table 11.3 The physical and chemical properties of biochars synthesized from different feedstocks through various pyrolysis production methods

Biochar feedstock	*T* (°C)	C	N	H	O	Yield (%)	Ash (%)	VM (%)	pH	SA (m^2/g)	CEC (cmol/kg)	Reference
Algae residues	300–700	50.5	10.5	7.54	30.8	40–90	4.8	–	–	–	–	IPCC (2013)
Bamboo	600	80.9	0.15	2.43	16.5	–	–	–	7.9	470.4	–	Lehmann (2009)
Municipal sludge	500	17.5	1.54	0.7	10.5	63.1	74.2	–	8.8	–	76.8	Qian and Kumar (2015)
Corn stover	600	70.6	–	–	–	–	16.7	23.5	9.42	527	252.1	Menendez et al. (2010)
Cow manure	500	43.7	–	–	–	57.2	67.5	17.2	10.2	21.9	149	Inyang et al. (2016)
Domestic wastewater sludge	400	42.7	8.1	3.4	8.1	–	37.1	34.5	7.3	–	–	Goyal et al. (2008)
Grass	400	77.3	1.24	4.70	16.7	37.2	16.3	26.8	–	8.7	–	Kastner et al. (2012)
Hickory wood	600	81.8	0.73	2.16	15.3	–	–	–	8.4	401.0	–	42
Japanese cedar	400	72.0	1.6	4.2	22.1	–	0.1	57.7	7.7	–	–	33
Municipal sludge	500	17.5	1.54	0.7	10.5	63.1	74.2	–	8.8	–	76.8	45
Oak wood	600	87.5	–	–	–	–	1.30	27.5	7.9	642	75.7	Menendez et al. (2010)
Peanut hull	600	86.4	0.94	1.36	11.3	–	–	–	6.9	27.1	–	Lehmann (2009)
Pig manure	500	42.7	–	–	–	38.5	48.4	11.0	10.5	47.4	82.8	Inyang et al. (2016)
Pinewood	450	81.4	0.3	3.0	15.3	41–44	4.6	8.2	–	166	–	Kan et al. (2016)
Poultry litter	600	23.6	–	–	–	–	55.8	44.1	10.3	94	58.7	Menendez et al. (2010)
Rice	400	37.2	1.3	1.2	12.4	–	47.9	38.2	6.7	–	–	Goyal et al. (2008)
Sugarcane bagasse	600	76.5	3.03	2.93	19.8	–	–	–	7.5	557.4	–	Lehmann (2009)

Walnut shell	900	55.3	0.47	0.89	1.6	–	40.4	–	9.7	227.1	33.4	Kasozi et al. (2010)
Wheat straw	450	65.2	0.9	2.3	31.5	41–44	3.9	7.2	–	184	–	Kan et al. (2016)
Wood (*Pinus ponderosa*)	400	74.1	0.06	4.95	20.9	35.3	1.4	36.4	–	28.7	–	Kong et al. (2011)

T pyrolysis temperature, *VM* volatile matter (%, dry basis), *SA* surface area, *CEC* cation exchange capacity volatile organic compound losses and to increase in the basic cations in biochar produced at high temperatures. In addition, biochar produced at lower temperatures may contain greater densities of acidic functional groups (i.e., phenolic and carboxylic groups), which may be a reason for decreasing biochar pH (Shaheen et al. 2018).

11.1.2.3 Factors Affecting Biochar Properties

The reaction conditions during the pyrolysis process are mainly responsible for producing biochar. The factors such as feedstocks, temperature, size of the particle, heating rate, etc. mainly influence biochar properties. The detailed knowledge of analyzing biochar properties is important for determining the biochar application. Various biomass from different sources such as plant materials, agricultural residues, biomass from wood, solid wastes, etc. has been used for producing biochar (Zhang and Sun 2014).

Types of Wood

Biomass is considered as a complex solid material composed of biological, organic, or inorganic material which was derived from living or living organisms. Biomass is characterized into two types:

1. Woody biomass
2. Non-woody biomass

Woody biomass essentially includes tree residues and forestry residues (Zhu et al. 2015). The attributes of wood biomass are low dampness, low debris, less porosity, high density, and calorific value. Non-woody biomass comprises animal waste and industrial and agricultural solid wastes. The attributes of non-woody biomass are high debris, high dampness, high voidage, low density, and calorific value. Among different attributes of biomass feedstock, moisture content has a great impact on biomass formation. The moisture in the biomass can exist in different forms, such as liquid water, and water vapor is adsorbed within the pores of biomass. Higher moisture content in biomass majorly inhibits the formation of char and raises the amount of energy needed to attain the pyrolysis temperature. Low moisture content in the biomass is preferable for biochar formation because of the impressive decrease in the heat energy and the reduction of time needed for the pyrolysis process, which makes that biochar formation economically feasible when compared with biomass with high moisture content.

Carbonization Temperature

Pyrolysis is the most famous method for exchanging biomasses over to biochar through the thermochemical decay process under an oxygen-denied environment at the raised temperature. Contingent upon the conditions, pyrolysis cycles can be grouped into three fundamental classifications: (1) slow pyrolysis (temperatures <300 °C), (2) moderate pyrolysis (temperatures of 300–500 °C), and (3) quick pyrolysis (temperatures more prominent than 500 °C). Pyrolysis temperature influences physicochemical properties and structure of biochar, for example, elemental components, pore structure, surface area, and functional groups (Lee et al. 2017). The impact of pyrolysis temperature on such properties can be attributed to the influx of volatiles at high temperatures.

Residence Time

Expanding the residence time at low pyrolysis temperature (300 °C) brought about a slight decrease in biochar yield and reformist expansion in pH and iodine adsorption number of biochar. Nonetheless, expanding residence time at high pyrolysis temperature (600 °C) had little impact on biochar yield or pH, while it diminished the iodine adsorption number of biochar (Lehmann and Joseph 2009).

Pre-treatment of Biomass

Pre-treating the biomass before pyrolysis influences biochar characteristics. The common pre-treatment methods available are immersing the raw materials in solution and particle size reduction of biomass. The reduction of biomass particle size results in high biochar yield. For example, pinewood biomass was pre-treated by immersing the biomass in a dilute acidic solution. Pre-treatment methods such as nitrogen and metal doping can influence biochar production, and solution pre-treatment such as soaking or steaming can influence the elemental composition and properties of biochar, while the baking method can increase the carbon content and reduce the oxygen and moisture content of biochar (Lehmann and Joseph 2009). The potential biomass for biochar generation is utilized either independently or as mixes. Contingent upon the innovation utilized, the practical execution is as often as possible restricted by the moisture or mineral substance of the biomass. For example, the presence of chlorine and soluble base metals can cause consumption. Because of various production technologies and biomass, the properties of the produced biochar can go broadly. While components, for example, hydrogen (H), O, nitrogen (N), and sulfur (S), are volatilized during pyrolysis, minerals, for example, phosphorus (P), K, calcium (Ca), magnesium (Mg), and silicon (Si), remain, and their concentrations increment in the resultant biochar. The occurrence of harmful compounds or components in biochar can either be an outcome of polluted biomass during pyrolysis/gasification (You et al. 2018).

11.1.2.4 Characterization of Biochar

Biochar characterization is performed to determine the ability to remove pollutants or other applications. The structural and elemental analysis also helps to predict the impact of biochar on the environment. In addition, the metals interact with biochar which is a function of pH, as (1) the function of biochar differs with pH and (2) metal contaminant ion speciation varies with pH. These characteristics of biochar showed the ability to act as a highly efficient adsorbent for removing most of the soil pollutants. The structure, surface functional groups, and elemental analyses are used to characterize biochars (Li et al. 2019). Currently, numerous modern characterization techniques have been reported for characterizing biochar, such as scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), nuclear magnetic resonance

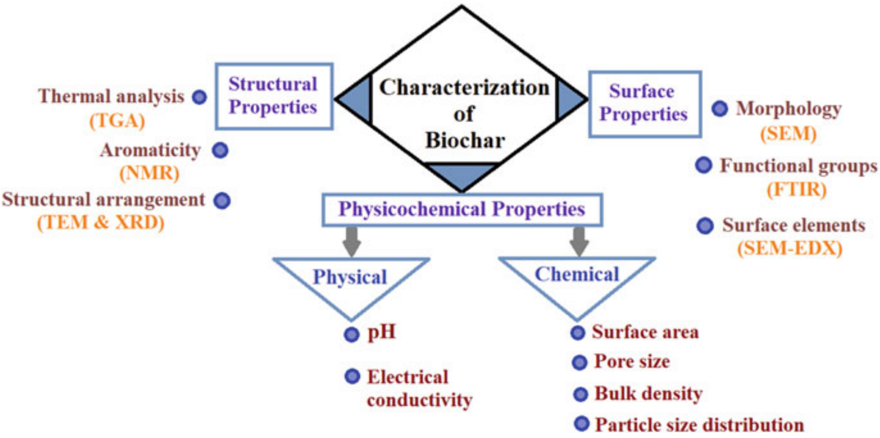


Fig. 11.2 Biochar characterization

(NMR) spectroscopy, Brunauer-Emmett-Teller (BET), proximate and ultimate analysis, Raman spectroscopy, etc. as shown in Fig. 11.2. The surface functional groups are characterized using Fourier transform infrared spectroscopy (FTIR). The biochar produced at different temperatures showed a significant difference in their surface functional groups. Apart from FTIR, NMR (nuclear magnetic resonance) can also be used for determining surface functional groups present in biochar. Physicochemical, surface, and structural characterization of biochar and the surface morphology before and after adsorption process can be predicted using SEM. X-ray diffraction is a broadly relevant strategy to determine the crystallinity and structure of biochar. TGA is applied for thermal analysis to observe the physical and chemical properties of materials which are measured as a function of a temperature rise. The surface area of biochar can be examined using BET analysis. The structural composition of biochar can be examined using a specific spectroscopic technique NMR (Yaashikaa et al. 2020).

The physicochemical properties of biochar strongly influence the role of biochar in several applications such as fuel cells, biosorption, agriculture, supercapacitors, catalyst/support, and environmental remediation. It was identified through research efforts that the properties of biochar can be altered using various chemical or physical agents to suit various applications.

11.1.2.5 Biochar and Bioenergy Production Process During Pyrolysis

Several methodologies can be utilized to produce biochar, including flash carbonization, gasification, pyrolysis, hydrothermal carbonization, and torrefaction (Lima et al. 2010). Among these methods, the most common and widely employed technique to produce biochar is pyrolysis. In the pyrolysis process (Fig. 11.3), temperatures above 300 °C are used to heat the biomass in the absence of O_2. During this process, the organic constituents are thermally decomposed into the vapor phase, whereas the final solid phase remains as biochar. The vapor phase is

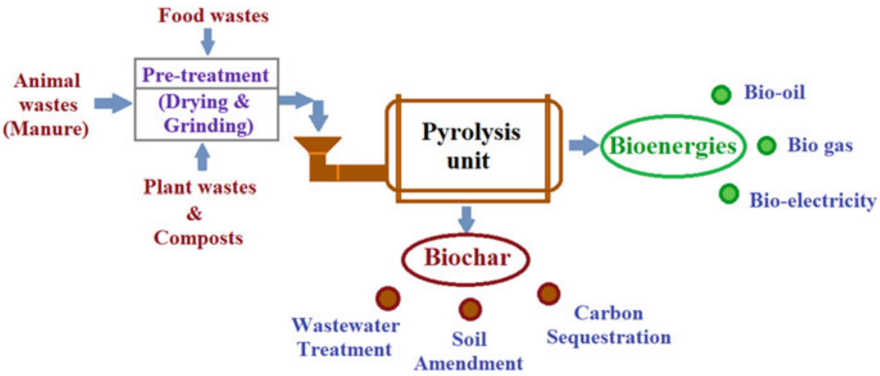


Fig. 11.3 Biochar and bioenergy production process during pyrolysis

cooled to generate bio-oil, in which high molecular weight and polar compounds are condensed. On the other hand, the volatile low molecular weight compounds (such as CH_4, H_2, C_2H_2, and CO) persist in the gas phase. Based on the differences in the rate of heating, pyrolysis can be classified into slow and fast pyrolysis. Fast pyrolysis involves heating the biomaterial (pyrolysis) at a faster rate (typically >300 °C/min) for a short residence time (typically less than 60 min) in the absence of oxygen. This process generally yields syngas (low-energy-density gas), bio-oil (high-energy-density liquid), and biochar.

In general, a very high yield of 50–70% bio-oil and low yields of 10–30% biochar and 15–20% syngas can be achieved through fast pyrolysis (Lu et al. 2012). On the other hand, slow pyrolysis involves heating the biomaterial (pyrolysis) over a varied temperature range (300–800 °C) at a slower rate (typically >5–7 °C/min) for a prolonged residence time (typically greater than 60 min) in the absence of oxygen. This process generally produces more biochar than fast pyrolysis. In general, around 35% syngas, 30% bio-oil, and 35% biochar can be expected through slow pyrolysis (Bartoli et al. 2016). In recent years, microwave-assisted pyrolysis has been garnering significant attention and often portrayed as a promising alternative to traditional pyrolysis methods (IPCC 2005). This is due to their inherent advantages such as uniform, selective, and volumetric heating, enhanced energy efficiency, and rapid rate of heating (Malghani et al. 2013).

Haeldermans et al. (2019) compared traditional and microwave-assisted pyrolysis for the production of biochar. The results indicated that microwave-assisted pyrolysis produced biochar with a higher degree of aromaticity at lower temperatures than conventional pyrolysis. Also, microwave-assisted pyrolysis offers more control over operation through instant off/on control as well as increases the quality and yield of biochar. Additionally, the process is environmentally benign as it decreases the formation of dangerous products as well as reduces the emission of contaminants. This is because microwave pyrolysis involves volumetric heating of the feedstock via bulk energy transfer, whereas traditional heating involves heat transfer by convection, radiation, and conduction (McKendry 2002).

Table 11.3 summarizes the impact of feedstock on the biochar properties. Significant variations can be observed on important properties, including CEC, surface area, and yield (%). The surface area of bamboo-derived biochar pyrolyzed at 600 °C (470.1 m^2/g) was found to be much higher than that of pig manure biochar (47.4 m^2/g) at the same pyrolysis temperature. On the other hand, municipal sludge biochar exhibited smaller CEC (76.8 cmol/kg) than cow manure biochar (149 cmol/kg) at a pyrolysis temperature of 500 °C.

The foremost cause of the crisis is greenhouse gas emissions, with CO_2 being the most common of these gases. As a result of human activity, atmospheric CO_2 levels have increased from 280 parts per million before industrialization to 360–396 parts per million now (Mohan and Pittman 2006). The use of biomass to produce energy, power, liquid fuels, hydrogen, and value-added chemicals with lower greenhouse gas emissions is gaining popularity around the world. Pyrolysis and gasification are emerging as promising biomass utilization technologies with a positive environmental impact.

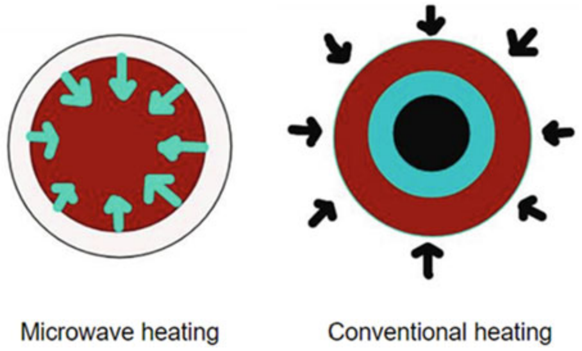
Biomass pyrolysis is a thermal degradation process that produces various gaseous and aqueous products as well as char residue in the absence of oxygen or air (Mohan et al. 2011). Endothermic pyrolysis reactions typically require direct or indirect heating from hot gases, hot solids, liquid heat transfer media, oxidation, and partial oxidation reactions. Microwave-assisted pyrolysis (MWP) has been shown to be a promising alternative to conventional pyrolysis (CP) in recent decades, owing to its fast heating rate, selective heating, and volumetric and coherent heating that all make a significant contribution to accelerating reaction rates and increasing energy efficiency. Microwave heating (MWH) simplifies operation by providing instant on/off control and improves product yield and quality. Furthermore, it reduces the formation of toxic materials and the presence of contaminants, making the technique environmentally sustainable (Müller-Stöver et al. 2012; Jafri et al. 2018; Nartey and Zhao 2014; Masek et al. 2013).

Biomass is usually a low microwave (MW) absorber. However, the presence of relatively high moisture and inorganic substances can improve MW absorption capacity. The MWP of biomass has been investigated without microwave absorbers (MWAs), with MWA and inorganic additives. The use of MWAs improves pyrolysis temperature at relatively low power. The MWAs can indirectly heat surrounding biomass particles, influencing product yield and its quality. MWAs and some catalysts added to biomass can adjust products distribution, increase process energy efficiency, or improve the contents of specific components in bio-oil, gas, and biochar under different conditions (Oh et al. 2017; Basu 2010; Senthil Kumar et al. 2011, 2013; Yaashikaa et al. 2019; Xie et al. 2014; Qambrani et al. 2017; Qiu et al. 2009).

Microwave Pyrolysis and Traditional Biomass Pyrolysis

In the microwave heating process, the microwave penetrates into the feed particle, and then the microwave energy is transformed into thermal energy inside the particle

Fig. 11.4 Difference between microwave heating and conventional heating mechanisms



because of the interaction of molecules with the electromagnetic field. The thermal energy after constantly accumulating inside the biomass continues to transfer outwards due to the heat loss effect on the surface of the particle. In the conventional electrical heating process, the heat is transferred from the high-temperature gas to the biomass particle surface through a convection mechanism, and it is then further transferred from the outside surface of the body to the inside core through a conduction mechanism. The following Fig. 11.4 shows the difference between microwave heating and conventional heating mechanisms (Demirbas 1997).

Microwave heating is preferred over conventional heating due to the following reasons:

- In-core volumetric and uniform heating at the molecular level in microwave heating, whereas in conventional heating, superficial heating is done through conduction, convection, and radiation; hence, its rapid, efficient, and high electricity conversion efficiency takes place.
- In microwave heating, the process is selective and dependent on material properties, but precise and controlled heating can be done; therefore, the process is flexible.
- Other advantages include the usage of portable equipment, production of lesser contaminants, lower thermal inertia, and faster response.

It not only absorbs microwave energy but also functions as catalysts in the reactor, interacting with gas, vapor, and particles and changing product distribution and quality. The highest biochar output was reported to be >60 wt% for MWP, while the maximum BET surface area was around 450–800 m^2/g. The current state of technology and the economics of biomass MWP in China were briefly discussed. The feedstock qualities, reactor types, operating settings, MWAs, and catalysts added to the system all play a role in optimizing biochar yield and quality.

MWH is a unique technique and offers several advantages over conventional heating based on previous research, such as more controllable, high energy efficiency and cost-effectiveness. MWH offers a potentially attractive alternative to CP

Table 11.4 Advantages and disadvantages of conventional and microwave-assisted pyrolysis (Jing Li et al. 2016)

Conventional pyrolysis (CP)		Microwave-assisted pyrolysis (MWP)	
Advantages	Disadvantages	Advantages	Disadvantages
Simplicity in design and operation; flexibility of feedstocks and products; well-developed and easy scale-up	Low-quality products; energy consumption due to high temperature (greater than 600 °C)	Fast, uniform, volumetric heating; high-quality products; reduced processing temperature and energy savings; less feedstock pre-treatment needed; non-thermal effects; increase the pre-exponential; decrease the activation energy	Relatively different temperature measurements; uncertain economics of the process scaling up; limited by available microwave technologies and large-scale process difficulties; microwave absorbers needed

systems owing to its energy transfer rather than heat transfer, non-contact and rapid heating, selective and volumetric heating, high level of safety, as well as quick startup and shutdown. Numerous results have shown that MWH is better than conventional heating to carry out biomass pyrolysis.

Generally, the difference between microwave and conventional heating can be mainly attributed to their different heating mechanisms (dielectric heating vs. convective and conductive heating) and to the occurrence of a hot spot (spark) generated by MWH. Several researchers looked at MWP in comparison with CP and identified considerable differences between the two technologies (e.g., char yield, see Fig. 11.1), emphasizing decomposition temperature, heating rates, and requirements for feedstock preprocessing (e.g., shredding or drying) (Gayathri et al. 2021; Saidur et al. 2011).

The presence of water in biomass feedstocks may decrease the heating rate for CP because water is expected to absorb energy, reducing the heating rate and the final temperature of biomass pyrolysis. However, the presence of water in biomass may increase the heating rate of MWP, due mainly to the large MW absorption capacity of water in comparison with dry biomass itself. CP of biomass sometimes needs catalysts to enhance the breakdown of large molecules into small-molecule products, including tar cracking and/or reforming.

MWP of biomass not only needs catalysts but also requires MWAs because biomass is generally not a good absorber of MW. Pre-treatment and blending with MWAs can increase the healing rate and improve the yield and quality of specific products. It should be noted that MWAs may also act as catalysts, accelerating the reaction rate by differentiating the reaction path and thus decreasing the energy of activation (Barreto 2018). It was reported that direct critical comparison of MWP and CP might not be appropriate due to the presence and functions of MWAs (Table 11.4) (Rajapaksha et al. 2016).

11.1.2.6 Modification of Biochar

Although several inherent properties of biochar can be used to suit various applications, they can be further modified to enhance their efficiency. In the field of biochar modifications, the majority of research has been focused on preparing modified biochars for the sorption of various contaminants/nutrients. In general, it was established that the sorption performance of biochar is inferior to various well-established biosorbents or activated carbon. One of the major applications of biochar in the soil is to act as a nutrient supplier and to enhance soil fertility. Therefore, it is critical that the sorption performance of biochar be optimized to achieve its full potential (Rajapaksha et al. 2016). For this purpose, several physical and chemical agents are utilized as described below.

Physical Modification

For the synthesis of biochar, physical modification methods are frequently employed as they are generally simple and economical; however, they are less effective than chemical modification techniques.

Steam Activation

With the aid of the steam activation method, synthesized biochar could be converted to activated biochar with high surface area and enhanced carbonaceous structure. Steam activation is generally carried out when the initial pyrolysis process, conducted at moderate temperatures (400–800 °C) in an O_2 absent atmosphere, is accompanied by a subsequent step in which the synthesized biochar is exposed to steam for partial gasification. This step stimulates crystalline C formation and partial devolatilization in biochar (Hemavathy et al. 2020).

With the help of the steam application, the biochar properties can be altered through the removal of the trapped products formed during incomplete combustion in thermal treatment. In particular, the process can develop new pores as well as widen the size of smaller pores developed during pyrolysis (Mani et al. 2013). By applying steam activation on whitewood, Azargohar and Dalai (2008) observed a significant increase in surface area from 10 to 664 mg/g. This enhancement of surface area is due to corrosion of biochar surface as well as generation of additional syngas, particularly in the form of H_2 (Varjani et al. 2019). Also, the process of steam activation removes trapped products (volatile gases) and thereby improves the volume of pores on the biochar surface as well as accessibility and development of internal pores.

Gas Purging

Gas purging also enhances the pore volume and surface area of biochar (Saeed et al. 2005). To be precise, CO_2 modification alters biochar surface by creating microporous structures owing to the fact that CO_2 could react with C of the biochar sample to form CO (i.e., hot corrosion) (Salih et al. 2011). Kim et al. (2019) observed that the pore volume (total) and surface area of biochar derived from oak wood under CO_2 environment were twice in value compared to the same biochar synthesized under N_2 environment. Alternatively, Zhang et al. (2016) performed CO_2–NH_3

modification on soybean straw biochar that combines the merits of NH_3 ammonification and CO_2 activation. The process enhanced the addition of new nitrogen functional groups on the soybean straw modified biochar as well as improved the development of micropore structure.

Chemical Modification

Acid/Base Modification

Through this modification, modulation of surface acidities and porous structure of biochar can be achieved. After modification using chemical agents such as HCl, H_2SO_4, HNO_3, NaOH, and KOH, El-Hendawy (2003) determined that HNO_3 modification resulted in enhanced sorption as well as pore diffusion of hydrated Pb(II) with O_2 groups and thereby increased the hydrophilic nature of biochar.

Functional Group Modification

The hydrophilicity and surface binding groups of biochar can be chemically tailored for the removal of specific contaminants at a specific rate from wastewaters as well as soil additives for polluted areas (Das et al. 2014). It is well known that the alteration of binding sites on the surface of sorbent influences the sorption capacity by several folds. Amine, carboxyl, phosphonate, hydroxyl, and phenolic groups are well-established binding sites for the sorption of various dyes/metals (Mohanty et al. 2018; Shaheen et al. 2019). If the proportion of these binding is limited, the resultant biochar materials exhibit inferior pollutant uptakes. However, several modification methods are available to enhance the density of these binding groups on the biochar surface.

Impregnation with Mineral Oxides

Biochar can also be engineered for specific applications via the impregnation of minerals. Yao et al. (2011) enhanced the functionality of biochar by distributing clay particles in biochar matrix. The authors mixed the biomass (hickory chips, bagasse, and bamboo) with clay and subsequently pyrolyzed at 600 °C in the absence of O_2 for 60 min. Due to the highly porous structure and presence of clay, the sorption capacity of biochar clay composites towards methylene blue improved fivefold compared to virgin biochar.

11.1.2.7 Applications of Biochar

The application and efficiency of biochar in various fields depend on the type of biomass used for producing biochar. The characterization of biochar is very important for determining biochar elemental composition, surface functional groups, stability, and structure. The common thermochemical techniques used for biochar production include pyrolysis, hydrothermal carbonization, gasification, flash carbonization, and torrefaction (Sun et al. 2011; Teixidó et al. 2011). Of all these methods, pyrolysis is the most commonly used to produce biochar. Biochar has been employed in agricultural fields also for eliminating soil pollutants. Many agricultural residues have been utilized for producing biochar, such as rice straw (Tong et al.

2011), wheat straw (Qian et al. 2019), waste wood (Twidell 1998), sugar beet tailings (Uchimiya et al. 2010), corn cob (Budarin et al. 2010), etc. These biomasses are composed of mostly cellulose, hemicellulose, and lignin components.

The eco-friendly, inexpensive, and ease of preparation from various biomass using thermochemical techniques for addressing vast environmental applications makes biochar an intensive area of interest among researchers. The type of biomass and pyrolysis temperature influence how effective biochar is at eliminating toxins and pollutants from soil and the aquatic environment. The carbon-rich biochar produced using high pyrolysis temperature has more removal efficiency of organic pollutants due to its enriched properties such as porosity, surface area, pH, less dissolved carbon content, and hydrophobic nature.

Similarly, the biochar produced using lower temperature possesses oxygen-containing functional groups and high dissolved organic carbon and is less porous, so these types of biochar are more suitable for removing inorganic pollutants. Other factors like pH and residence time also contribute to the removal capacity of biochar. Biochar can also be used for other applications such as catalysts, wastewater treatment, composting, energy storage, carbon sequestration, and soil amendment. The advantages and limitations of different applications of biochar are listed in Table 11.5.

Biochar Application in Water and Wastewater Treatment

Biochar is a solid material with a high surface region and high porosity, properties that make it an appealing alternative in wastewater treatment. Biochar has been accounted to be a successful medium for catching supplements from wastewater, and that can be connected to the soil as an alteration. Biochar is accounted for to emphatically build toxin expulsion in wastewater because of its high porosity and high adsorption properties that enable poisons to aggregate on its surfaces, bringing about a clean effluent and supplement-rich biochar.

There is a rising pattern in the utilization of carbonized materials and crude biowaste in wastewater treatment. Many researchers played out a meta-examination to think about the ecological and monetary exhibition of biochar and activated coal in the evacuation of toxic contaminants. The examination revealed that evacuation execution of biochar to that of activated coal. It is in this manner supported that while the huge surface territory of activated coal favors toxin adsorption by pore filling, there are different elements, including surface functional groups, that clarify the removal execution of biochar.

Biochar can be used directly in water and wastewater treatment as a sorbent for pollutants removal or inbuilt wetlands (CWs) and the soil to improve water quality. Carbonaceous materials have long been employed as sorbents in soil and water to remove organic and inorganic pollutants (Wang et al. 2006; Wiedner et al. 2013; Hu et al. 2017). The most often used carbonaceous sorbent is activated carbon, which is charcoal that has been treated (i.e., activated) with oxygen (in general) to enhance microporosity and surface area. The term "activated" refers to the increased surface area of charcoal as a result of thermal or chemical treatment.

Table 11.5 Advantages and limitations of different applications of biochar

Applications	Aim	Benefits	Limitations	References
Catalyst	Act as supporting materials for direct catalysis	Low cost, more functional groups, large surface area	Efficiency may be less	Dhyani and Bhaskar (2018), Vamvuka et al. (2003), Van Poucke et al. (2016)
Energy storage	Utilizing as electrode materials	Low cost, highly porous, large surface area	Performance is low	Verheijen et al. (2010)
Soil amendment	Enhancing soil fertility and quality and carbon sequestration	Low cost, minimize the emission of greenhouse gases, helps to retain nutrients and water, controls nutrient loss	Contamination of heavy metals and polyaromatic hydrocarbons may persist	Vijayaraghavan and Ashokkumar (2019)
Adsorbents	Removal of organic and inorganic pollutants in soil and aqueous system	Low cost and more oxygen groups present in biochar enhance the adsorption of pollutants	The removal efficiency of pollutants is underdetermined, and heavy metals remain in the soil	Vijayaraghavan et al. (2011)
Composting	Improving the structure of microbial population and carbon mineralization	Reduces the emission of greenhouse gases on a large surface area and retains nutrients	There may be a chance of heavy metals and other contaminants invading the soil	Wahi et al. (2017)

Remediation of Organic Contaminants in Water

Researchers have been drawn to biochar because of its similarity to activated carbon in terms of organic pollutant elimination in water treatment and soil remediation (Zhao et al. 2013a, b). Table 11.6 summarizes recent studies on biochar applications for the remediation of inorganically and organically contaminated water (Zhao et al. 2010; Wang et al. 2009; Xiong et al. 2013; Duan et al. 2019). The electrostatic interactions between organic pollutants and biochar, as well as partitioning or adsorption, are crucial for remediation applications and are explored in detail in the following sections.

Remediation of Inorganic Contaminants in Water

Mining, smelting, metal finishing, fertilizers, animal dung, pesticides, leaded gasoline, battery production, power plants, wastewater, and sewage sludge are all examples of anthropogenic sources of inorganic pollutants in the environment. Metals, unlike organic pollutants, are non-biodegradable and highly harmful to

Table 11.6 Biochar utilization for organic and inorganic contaminant remediation in water

Contaminant (organic and inorganic)	Biochar type	Matrix	Effect	References
Atrazine	Dairy manure (200 °C)	Water	Partitioning into organic C/sorption	Xu et al. (2012)
Atrazine and simazine	Green waste (450 °C)	Water	Adsorption and partition	Fernandez and Menendez (2011)
Chlorpyrifos and fipronil	Cotton straw (450 and 850 °C)	Water	Because of the increased surface area and microporosity, adsorption occurs	Yao et al. (2011)
Deisopropylatrazine	Broiler litter (350 and 700 °C)	Water	Because of the huge surface area and aromaticity, there is a lot of absorption; sorption on noncarbonized fraction	Yu et al. (2014)
Norflurazon and fluridone	Grass and wood (200–600 °C)	Water	Sorption on amorphous C phase	Yakout et al. (2015)
Sulfamethoxazole	Bamboo (450 and 600 °C)	Water	Sorption	Yang et al. (2007)
Catechol and humic acid	Hardwood, softwood and grass (250, 400, and 650 °C)	Water	Adsorption due to presence of nanopores	Yang et al. (2010)
Naphthalene	Orange peel (250, 400, and 700 °C)	Water	Adsorption and partition	Zhang et al. (2017)
Pyrene	Corn stover (600 °C)	Water	Adsorption due to nanoporosity	Yao et al. (2012)
Chromium	Oakwood (400–450 °C)	Water	Sorption	Yao et al. (2014)
Copper	Crop straw (400 °C)	Water	Adsorption due to surface complexation	You et al. (2017)
Copper and zinc	Hardwood (450 °C)	Water	Endothermic adsorption	Du et al. (2011)
Lead	Dairy manure (200 °C)	Water	Precipitation with phosphate	Yao et al. (2014)
Lead	Sewage sludge (550 °C)	Water	Adsorption due to cation release, functional groups complexation, surface precipitation	Zama et al. (2017)
Mercury	Soybean stalk (300–700 °C)	Water	Precipitation, complexation, and reduction	Zhang et al. (2013)
Copper, cadmium, nickel, and zinc	Broiler litter (500 °C)	Water	Adsorption onto inorganic fraction of biochar	Zhang et al. (2016)

living beings due to their bioavailability. Carbonaceous materials have been utilized on purpose to remediate metal-contaminated soil and water in situ. Biochar has recently been used to adsorb metals in soil and water as a novel carbonaceous material.

11.2 Conclusions and Future Work

An application of activated biochar for removing particular pollutants is another specific way of using biochar as a renewable resource to address environmental problems. There is a need for further research to identify new methods of activating and deactivating biochar and to understand the adsorption and desorption mechanisms of various pollutants. Life cycle analysis is necessary to evaluate the economic impacts and environmental impacts of biochar.

New techniques have allowed for the advancement of biochar characterization methods. Optimizing the properties and activation of biochar is vital to obtaining maximum efficacy. The availability and economic viability of new technologies influence their utilization. Since biochar has emerged as an alternate source, standard characterization procedures must be implemented for a better understanding of biochar properties. Production of biochar uncovers a wide variety of biomass that has been utilized as the feedstock and pyrolyzed by various procedures to handle water pollution. The properties of resultant biochar are significantly influenced by pyrolysis temperature, feedstock, and pyrolysis technology. Because of its quick, volumetric, uniform, and selective heating, microwave-based technology has already been effectively applied in biomass pyrolysis for biochar formation. They not only absorb microwave energy but also function as catalysts in the reactor, interacting with gas, vapor, and solids to modify product distribution and quality.

However, most the MWAs may remain in biochar, and the effects of MWAs on biochar characteristics deserve more efforts to research. Biochar can be utilized as a major source for the expulsion of toxic pollutants. Biochar presents an abundant number of surface functional groups such as hydroxyl, methyl, carbonyl, and carboxyl. Many factors can affect its structure such as the high carbon content, oxygen-containing aromatic functional groups, and its high porosity. Its porosity, its stable molecular structure, and its surface area favor the pollutants' adsorption on its surface (Chen et al. 2014a, b).

The existence of more carbonized matter in biochar favors the removal of organic contaminants having a functional group of oxygen and hydrogen (Ahmad et al. 2012). Though the efficiency of biochar depends on the type of biomass and pyrolysis conditions, the development of biochar in future is focused on fine sharpening on biochar properties. Thus, biochar appears as a highly promising option for pollutant removal.

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Declaration of Competing Interest The authors report no declarations of interest.

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