Realistic Approach for Bioremediation of Heterogeneous Recalcitrant Compounds

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Abstract

Rapid industrialization and urbanization over the past few decades has resulted in the massive contamination of the environmental resources such as air, water, and soil. A wide variety of industrial activities and operation such as discharge or dumping of effluents, accidental leakage and spills, and fugitive emission are responsible for contamination of environment. Heterogeneous compounds generated from industries include organic as well as inorganic anthropogenic compounds such as polycyclic aromatic hydrocarbons, alkyl benzenes (benzene, toluene, xylene, and ethyl benzene), volatile organic compounds, persistent organic pollutants, and oxyanions (nitrate, sulfate, chromate, etc.). Nowadays, management of these pollutants in industries with conventional methods is a highly challenging task due to their toxicity, mutagenicity, and carcinogenicity and their being recalcitrant to natural degradation. To overcome the challenges associated with the above heterogeneous compounds, a modified biodegradation method could be adopted for the effective elimination of these toxic recalcitrants and their derivatives from the industrial effluents. This chapter aims to describe the emission of recalcitrant from different industries, challenges, accessible treatment techniques with their merits as well as demerits, and realistic approach for treatment of heterogeneous compounds by modified sequential bioreactor system to achieve zero pollutant emission.

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11.1 Introduction

Water is a tremendously available natural resource on the earth. Owing to huge industrialization and urbanization, water pollution becomes a worldwide problem. According to the United Nations world population prospects 2017 revision, the current world population is 7.6 billion which is expected to be 8.6 billion in 2030 and 98 billion in 2050. Based on the population growth rate, requirement of clean and safe water will be more in the forthcoming years. Sustainable and clean water cycles are utmost priority policy of various countries in the world. Therefore, it is the essential requisite for present environment to protect the water from being polluted or to develop any cost-effective method. An illogical and rapid global human activity reverberates into environmental deterioration (Singh and Singh 2019). In the present scenario, enormous development of various types of industries gives rise to economic capital of country but at the same time led to the production of hazardous compounds which has caused global deterioration of ecosystem. These industries use huge amount of potable water for different kinds of industrial processes and release the wastewater which contains numerous hazardous pollutants which affect the flora and fauna. Nowadays, contamination of surface water, land water, ground water, sediments, and air due to their contact with hazardous and toxic chemicals is a serious issue throughout the world (Barcelo and Kostianoy 2016). Generally, pollution is caused by heterogeneous compounds such as organics (polycyclic aromatic hydrocarbons (PAHs), alkyl benzenes, volatile organic compounds (VOCs), persistent organic pollutants (POPs)), inorganics (oxyanions), nutrients, heavy metals, and several micro pollutants with its derivatives such as pesticides, antibiotics, disinfection by-products (DBPs), endocrine-disrupting compounds (EDCs), personal care products (PCPs), and pharmaceuticals (Bui et al. 2019). All of these pollutants are considered to be the most dangerous due to its intrinsic toxicity, recalcitrant behavior, and high exposure level to the environment. Therefore, these pollutants have been blacklisted and placed on priority list by several environmental protection agencies. However, there is no probability to stop the release of wastewater into the environment. The conventional treatment methods are feasible to reduce the harmful effects of these pollutants. The different physicochemical treatment methods such as chemical precipitation, adsorption, membrane separation process, advanced oxidation process, ozonation, and ion-exchange are available for removal of these toxic pollutants from the environment at full scale (Wang and Chen 2009). However, these treatment techniques have certain limitations depending on the compound to be removed and their efficiency. In that, certain compounds are removed completely by some methods, few compounds are not removed at all, and some are removed partially by these physicochemical treatment methods (Rajasulochana and Preethy

2016). The problems associated with these techniques can be overcome by biodegradation methods. Biodegradation or bioremediation becomes more popular nowadays because they are cost-effective, energy-saving, and eco-friendly for the treatment of wastewater. Bioremediation is a feasible technology for the removal of organic as well as inorganic pollutants by means of microorganism or detoxification of hazardous/toxic chemicals from the environment (Basha et al. 2010; Pandey et al. 2007).

The major goal of bioremediation technology is transformation of organic pollutants into their less toxic metabolites or mineralization into CO_2 and water. This microbiological process reduces the hydrocarbon concentration to permissible levels so that there will be any chance of an unacceptable risk to the environment/human health (Talley 2006). Since the last decades, plentiful research has been carried out in order to eliminate these hazardous contaminants from the environment by using appropriate treatment methods. The newer ones are applied additionally to the existing conventional treatment techniques. These methods essentially include an extra step or process or application in the earlier methods to achieve the complete removal of hazardous pollutants. In the last few years, intense research is carried out to investigate the applicability of such advanced treatment technologies not only to remove only organic and inorganic contaminants but also to remove microorganisms, antibiotic-resistant bacteria, viruses, and protozoa from wastewater. This chapter provides knowledge about recent updates in bioremediation of recalcitrant compounds, conventional methods available to treat these toxic recalcitrant compounds with their merits and demerits, and application of newly made technology in context to complete the removal of recalcitrant compounds from the environment.

11.2 Classification of Heterogeneous Compounds

The constituents of wastewater are generally classified as organic and inorganic. Inorganic compound in contrast to organic compound is a chemical compound lacking C-H bonds. Some inorganic compounds comprise of carbon or hydrogen atoms in their molecular structure that are often only considered as inorganics such as carbon dioxide (CO_2), carbon monoxide (CO), cyanides (CN^-), thiocyanates (SCN^-), carbides (C_2^-), carbonates (CO_3^-), water (H_2O), and hydrochloric acid (HCl). Mostly inorganic compounds consist of metallic constituents, but not all. In fact, the compounds which are inorganic in nature are found in majority in this universe. The major sources of inorganic compounds (metallic and nonmetallic) in the wastewater are derived from industrial activities, by the addition of mineralized water from wells and groundwater, mining activities, by the release of inorganic chemical wastes, from the farms and agricultural lands, transportation, etc. (Speight 2017).

An organic compound is defined as any chemical compounds which entail carbon and hydrogen atoms also termed as hydrocarbon together covalently linked with oxygen and nitrogen in some cases. In general, molecules of organic compounds are associated with living organism. These typically consist of proteins (40–60%), carbohydrates (25–50%), and oils and fats (8–12%). The broad classifications of heterogeneous compounds are described in the following sections.

11.2.1 Types of Organic Compounds

11.2.1.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons or PAHs are recalcitrant organic compounds comprising of two or more fused benzene rings in linear, cluster, or angular arrangements. Incomplete combustion at high temperature (500–800 °C) or involvement of organic molecules at low temperature (100–300 °C) results in the formation of PAH compounds. PAH in aquatic system comes from accidental leakage, oil spills, atmospheric deposition on sediments, and release of contaminated sediments. PAH generally occurs in oil, coal, and tar deposits. With the increase in molecular weight, their concentration decreases in water owing to their very less hydrophilic property, although they are still the most problematic substances as they pose toxicity threat on ecosystem due to their carcinogenic, teratogenic, and mutagenic nature (Haritash and Kaushik 2009).

11.2.1.2 Alkyl Benzenes

Alkyl benzene or monocyclic aromatics with saturated side chains constitute important class of hydrocarbons. The alkyl benzenes are derivative of benzene in that more than one hydrogen atoms are replaced by alkyl groups of various structures. They are considered as substitute of aromatic hydrocarbons (Francis 1948). The term BTX refers to the mixture of benzene, toluene, and three xylene isomers (ortho, meta, and para) and together comes under the category of aromatic hydrocarbons from the effluent of petroleum refining and petrochemical industries. If ethyl benzene is included in the mixture, the referred mixture is known as BTEX. Benzene, toluene, xylene, and ethyl benzene can be made by several processes. Nevertheless, huge amount of BTEX is produced from the recovery of aromatics during the catalytic reforming of naphtha in petroleum refinery industries. Also, formation of cracked naphtha by steam cracking of hydrocarbons is also responsible for the production of BTX compounds.

11.2.1.3 Volatile Organic Compounds (VOCs)

Volatile organic compound or VOC is any organic chemical compound that has a very high vapor pressure (> 1 mm Hg) at ordinary room temperature (25 °C). The high vapor pressure is due to its low boiling point which causes molecules to evaporate or sublimate at bulk. VOC is categorized in three different ways:

- Very volatile organic compounds (VVOCs)
- Volatile organic compounds (VOCs)
- Semi-volatile organic compounds (SVOCs)

More volatility of compounds is directly related to the higher degree of emission from the surface. Very volatile organic compounds are highly volatile in nature, hence it is difficult to measure, and are found mostly as gases in the air rather than in any kind of materials or on the surfaces. Propane, butane, and methyl chloride are examples of VVOCs (boiling point 50–100 °C), whereas formaldehyde, acetone, ethanol, and hexanol whose boiling point ranges from 50–100 to 240–260 °C are known as VOCs. SVOC boiling point ranges from 240–260 to 380–400 °C, and examples are pesticides, plasticizers, polychlorinated biphenyls (PCB), etc. (USEPA regulations 2019). Volatile organic compounds are of great environmental concern because being in a vapor state, it is very mobile and easily incorporated into the environment. In addition to that, the release of these compounds into public area like treatment plant causes severe effects to plant workers.

11.2.1.4 Persistent Organic Pollutants (POPs)

Persistent organic pollutants (POPs) are of global environmental concern owing to their persistence to environmental degradation, potential for long-term transport, accumulation in the food chain, as well as toxic adverse effects on human health and environment. In general, human being comes in contact with these hazardous compounds in several ways such as food, breathing of air, outdoors, and indoor workplace. POPs are contained in our usable products for daily living (flame retardants, surfactants) which are generally added in order to enhance the product quality. So, it can be said that POPs are available everywhere in this earth in considerable amount. The very much known examples of POPs are pesticides such as DDT, polychlorinated biphenyls (PCB), dioxins, and dibenzofuran. Human exposure to these compounds causes risk of cancer, reproductive disorders, disruption of immune systems, etc. (WHO database 2019; Morabet 2018).

11.2.2 Types of Inorganic Compounds

11.2.2.1 Nitrate

Nitrate, the most highly oxidized form of nitrogen, is an inorganic substance which is formed naturally when nitrogen combines with oxygen or ozone. Nitrogen is essential for the growth of microorganisms, plants, and animals because it works as nutrient or stimulator for them. It is a common contaminant of drinking water and creates serious health problems if present in excessively high concentrations (Seferlis 2008). Nitrate is commonly present in the surface and ground water because it is an end product during aerobic decomposition of organic nitrogenous matter. Significant sources of nitrates include fertilizers, animal feedlots, septic systems, industrial waste, food waste, and drainage from livestock feedlots.

11.2.2.2 Sulfates

In natural environment, sulfur is present in the form of pyrite (FeS_2) and gypsum in sediment ($CaSO_4$), whereas sulfates occur naturally in several minerals includes barite ($BaSO_4$) and epsomite ($MgSO_4.7H_2O$). Point sources of sulfates are sewage treatment plant and municipal or industrial discharge such as tanneries, pulp mills, and textile mills, runoff from fertilized agricultural lands, production of pharmaceutical products, fermentation process, and mining process. Sulfates are generally used in the production of fertilizers, dyes, soaps, shampoos, insecticides, fungicides, sedimentation agents, and plating industries (Klok et al. 2013; Jarvis and Younger 2000). Their solubility in water depends on covalent bonds with specific element like magnesium, potassium and sodium sulfates are more soluble, whereas barium and calcium sulfates and some heavy metals are sparingly soluble in water. Similar to carbon, nitrogen, and phosphorus cycle, a new platform of sulfur-based technologies incorporated with sulfur cycle was developed for the simultaneous removal of possible contaminants like sulfate, carbon, phosphorus, metals, and nitrogen from wastewater (Hao et al. 2014).

11.2.2.3 Heavy Metals

Heavy metals are naturally occurring substances which possess high atomic weight and density relatively more than water. By taking into consideration or assumptions that heaviness and toxicity are correlated, it also includes metalloids such as arsenic which is very toxic at low level of exposure. Environmental contamination by heavy metals nowadays becomes an ecological and global public health concern. Their multiple applications in various places such as industrial, agricultural, domestic, and technological application are responsible for the huge distribution in the environment. The effluent from mining regions generally contains lead, arsenic, copper, chromium, cadmium, and zinc. The release of these heavy metals into the environment leads to contamination of soil, water, and agricultural land (accumulation of metals on food crops and plants) (Verma and Kaur 2016). Among all the above-mentioned heavy metals, chromate is considered as one of the human carcinogen via inhalation. It has high environmental mobility, and it can develop from anthropogenic and natural sources. The major sources of chromium and its derivatives come from chemical industries, dye production, preservation of wood, leather tanning, manufacturing of various alloys, and chrome plating (Zhitkovich 2011).

11.3 Effluents from Various Industries

Tremendously, the main important sources of the pollution of environment are industrial effluent or discharge. A huge amount of wastewater is dumped into the rivers, coastal areas, lakes, and nearby water bodies. Based on different industries and contaminant, there are various types of industrial wastewater; each sector produces its own specific combination of pollutants (Walakira and Okat-okumu 2011). In general industries discharge two types of wastewater such as organic and inorganic industrial wastewater.

11.3.1 Inorganic Wastewater

The main source of industrial inorganic wastewater is coal and steel industry, electroplating plants, iron picking works, commercial enterprises, and nonmetallic industries. This wastewater comprises huge amount of heavy metals, suspended matter, less COD, slag, etc. Mainly inorganic wastewater is produced by the following industries:

- Electric power plants
- Battery manufacturing plant
- Iron and steel industry
- Mines and quarries
- Textile and leather industries
- Microelectronic plant

11.3.2 Organic Industrial Wastewater

Organic industrial wastewater chiefly entails organic waste from those chemical industries which use organic substances for incorporating chemical reactions. The organic wastewater can be removed by means of biological treatment. The industries producing organic wastewaters are as follows:

- Pharmaceuticals, organic dye-stuffs
- Pesticides and herbicides, glue and adhesives, textiles
- Tanneries and leather industries
- Pulp and paper and cellulose manufacturing plants
- Oil refining industries
- Petrochemical industries
- Food and dairy industries
- Brewery and fermentation factories
- Iron and steel industry

11.4 Toxic Effects of Heterogeneous Pollutants

In this section, the different types of organic and inorganic pollutants coming from various industries as well as their toxic effects are demonstrated. The receiving water bodies are polluted by the effluent discharged from industries rendering them

Table 11.1 Toxic effects of heterogeneous pollutants of industrial wastewater

Types of pollutants	Toxic effects
Polycyclic aromatic hydrocarbon (PAH)	PAH compounds are challenging pollutants in terms of removal as it is persistent in the environment due to its low solubility in nature. It affects the living organism due to their acute toxicity, carcinogenicity, and mutagenicity
Alkyl benzenes	They are toxic for living organism as it imparts unpleasant odor
	It adversely affects plant growth and reproductive capacity of the aquatic organism
Volatile organic compounds (VOC)	Short-term exposure: Headache, memory problem, visual disorders, dizziness, eye and skin irritation
	Long-term exposure: Damage of liver, kidney and central nervous system, cancer
Persistent organic pollutants (POP)	The discharge of POP-containing wastewater can pose serious health problems. It is considered highly poisonous and has acute toxicity on the living beings. Due to this the liver and respiratory and nervous systems can be damaged.
Inorganic dissolved salts	It stimulates the total dissolved solids concentration in water which ultimately cause scaling in water supplying pipes and unsuitable for irrigation purpose. They are harmful for aquatic life and toxic for human if above permissible limits
Heavy metals	Buildup of heavy metals cause immense effect on flora and fauna, skin rashes, gastrointestinal problem, fluorosis by fluorides, respiratory problems, etc.

unsuitable for drinking and any other purposes. Table 11.1 shows the adverse effects caused by various kinds of pollutants.

11.5 Physicochemical Treatment Techniques with Merits and Demerits

Generally, conventional wastewater treatment method comprises of a combination of physical and chemical processes for the removal of contaminates. The evolution of physicochemical process came in the late 1950s and at the start of 1960s. During that time for the removal of BOD and suspended solids sedimentation, sand filtration, various types of filters such as press, drum, and cartridge filters, coagulation and flocculation processes were used. In between 1980s and 1990s, absorption using activated carbon was adopted by some researchers for nitrification and BOD removal. In the past two decades, membrane processes such as micro-, ultra- and nanofiltration, reverse osmosis, and advanced oxidation process come into the scenario for possible removal of emerging pollutants in tertiary treatment (Dezotti et al. 2011). Different types of physicochemical treatment methods available for removal of heterogeneous pollutants with their merits and demerits are presented in Table 11.2.

Table 11.2 Merits and demerits of conventional methods used for treatment of polluted wastewater

Process	Merits	Demerits	References
Chemical precipitation	Very simple technology and equipment used in this process, economical and efficient at high loading of pollutants, integrated process, effective technique for removal of metals and fluoride, good for COD removal	Large amount of chemical requirement and consumption such as lime, hydrogen sulfide, regular monitoring of physicochemical properties, addition of extra oxidation step if metals are highly complexed, non-efficient in terms of removal of metal ions at low concentration, requirement of adjunction of unusable chemicals used in the treatment, high amount of sludge production	Duan and Gregory (2003), Fontela et al. (2011), Lefebvre et al. (2010) and Matilainen et al. (2010)
Chemical coagulation	It is an economical treatment process extensively used for removal of turbidity and color	More sludge production, not able to remove trace organics	Henze (2001) and Bratby (2006)
Floatation	Able to remove tiny and low-density particles which will require long settling time, ionic and non-ionic collectors, very useful for primary classification, require low retention time, used as a tertiary treatment of pulp and paper industry	Not cost-effective, large maintenance required, selectivity is dependent on pH, chemical required to control the hydrophobicity among the particles to maintain froth characteristics	Sharma and Sanghi (2012), Soune and Ghate (2004) and Forgacs et al. (2004)
Electrocoagulation	Adsorption and degradation can be achieved at the same time, efficient for removal of soluble and insoluble organics	Evolvement of secondary pollutants, comparatively high cost, less efficient in trace organics removal	Barrera-Diaz et al. (2011)

(continued)

Table 11.2 (continued)

Process	Merits	Demerits	References
Ion exchange	Easy to use with other techniques (integrated process), applicable to various flow regimes, well-established and tested technologies, variety of commercial products are available, ease of regeneration, very rapid and efficient physiochemical process, interesting for recovery of metals	Some economic constraints in terms of resin, maintenance, and regeneration cost, requires more spaces if more volume used, clogging of reactors due to rapid saturation, fouling of beads, rejection of resins	Anjaneyulu et al. (2005) and Baraket (2011)
Adsorption	Well-established tertiary treatment techniques, very simple technique, availability of wide range of commercial and natural adsorbents, very efficient process with rapid kinetics, any kind of pollutants organic or inorganics can be removed by this technique, simple equipment required	Nondestructive process, difficulty in regeneration of adsorbents, expensive disposal of potentially toxic spent adsorbent, desire various types of adsorbents, nonselective methods, elimination of adsorbents	Grover et al. (2011), Nguyen et al. (2012) and Ternes et al. (2002)
Advanced oxidation	Possesses efficiency for degradation of trace organics by generation of free radicals, simple, rapid and efficient process, color and odor are well removed, high throughput, no sludge generation, disinfection	Procurement of chemicals, proper management of oxidant, efficiency directly affects by type of oxidant, short half-life of ozone, pretreatment required for removal of solids, formation of toxic intermediate and by products	Belgiorno et al. (2007), Rojas et al. (2011) and Tuhkanen and Marinosa (2010)
Nanofiltration	Good removal in context of trace organics via electrostatic repulsion	Degree of complexity with separation process, formation of concentrated sludge, fouling	Alturki et al. (2010), Bellona et al. (2004) and Nghiem et al. (2004)

11.6 Bioremediation

According to United States of Environmental Protection Agency (USEPA), bioremediation is spontaneous or managed process which involves living microorganism to degrade or transformation of contaminants into less toxic or nontoxic forms, therefore remedying or eliminating from environmental (EPA 1994). The major goal of bioremediation is to stimulate organism with supplement of essential nutrients that enables them to detoxify or destroy the contaminants. Transformation of organic contaminants through microorganism normally occurs due to organism used pollutants or contaminants for self-growth and reproduction because it works as carbon source or food for them and it provides electrons so that organism can extract to obtain energy. Microorganism gains energy through catalyzing energy-releasing chemical reactions which involves breakdown of chemical bonds and transfer of electrons away from the environment. There are two types of bioremediation:

- In situ bioremediation: It refers to remediation at the point of origin. The advantage of in situ bioremediation is that it prevents the spreading of contaminants during transportation.
- Ex situ bioremediation: It refers to remediation when the contaminated waste has been removed from the treatment place. It helps to control the bioremediation products and making the contaminated area free for use.

11.6.1 Conventional Bioremediation Techniques/Reactors

11.6.1.1 Continuous Stirred-Tank Bioreactors (CSTB)

In the continuous stirred-tank bioreactor, the contents of the vessel no longer vary with time, so that microorganism remains in the bioreactor. The most successful continuous systems are with yeasts and bacteria, in that the desired products are the cells or primary metabolite of the compound. Activated sludge process is the most widely used CSTB process in wastewater treatment. Chemostat is a type of CSTB which is used to culture microorganism and study the basic biochemical properties of microbes. In this reactor, liquid is continuously introduced and taken off from the reactor. The main characteristic of ideal CSTB is that the concentration of microorganism and substrates is uniform everywhere throughout the reactor. It is generally used for anaerobic and aerobic treatment of high concentration of organic and inorganic mixtures (Rittmann and McCarty 2012). The removal of various hydrocarbons from industrial wastewater by using mixed microbial consortium in a CSTB is reported in the literature (Gargouri et al. 2011; Geerdink et al. 1996). The schematic representation of CSTB is shown in Fig. 11.1.

11.6.1.2 Fluidized Bed Bioreactors

In the fluidized bed reactor, attachments of microorganism to the carrier are maintained in suspension by upward flow rate of fluid which needs to be treated. The microorganisms attached to the substance are known as biofilm carriers. These may be granular activated carbon (GAC), sand grains, gravels, diatomaceous earth, or any other solids which are resistant to abrasion. Due to upward velocity of the fluid, carriers are in continuous suspension which depends upon the relative density of the carrier to water. The fluidized bed reactor has the advantage to continuously withdraw products and introduce reactants due to its nature of being fluidized. In

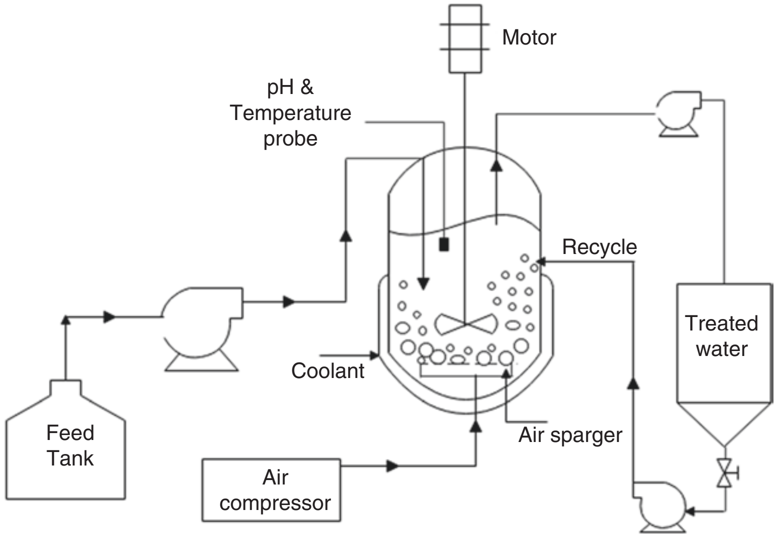


Fig. 11.1 Schematic representation of continuous stirred-tank bioreactor (CSTB)

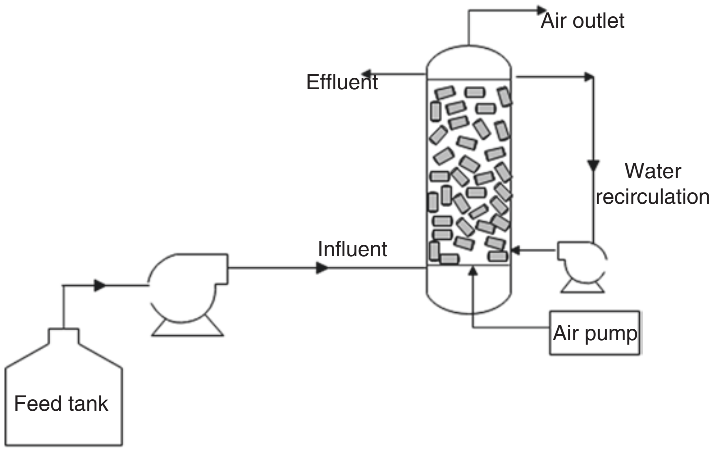


Fig. 11.2 Schematic representation of fluidized bed reactor

continuous process, this reactor allows the manufacturers to produce different products more efficiently rather than batch process. Fluidized bed bioreactors are extensively used for many industrial wastewater treatments such as petroleum wastewater, textile industry effluent, and real acid mine drainage water (Balagi and Poongothai 2012; Banerjee and Ghoshal 2016; Sahinkaya et al. 2011). The basic structure of fluidized bed reactor is shown in Fig. 11.2.

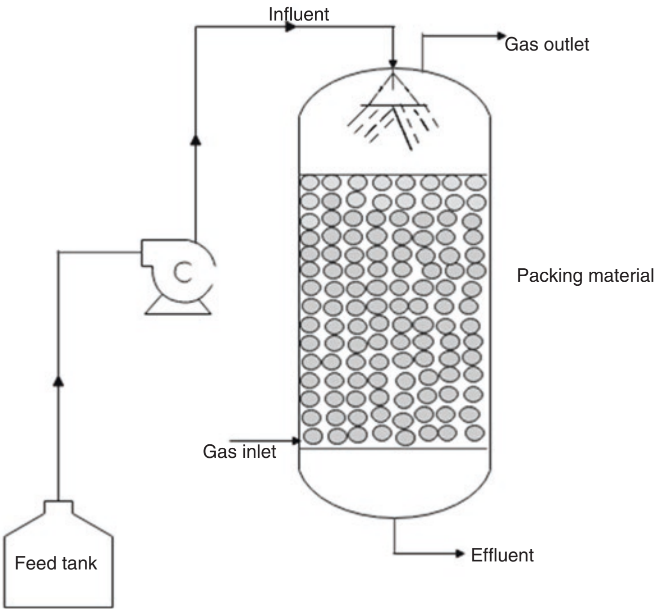


Fig. 11.3 Pictorial representation of packed bed reactor

11.6.1.3 Packed Bed Bioreactor

Generally, packed bed bioreactors are used for aerobic treatment of wastewater in the form of trickling filters. Packed bed reactor is the most common biofilm reactor in which carrier media are stationary. Various kinds of packed bed materials such as rock, slag, plastics, and ceramic can be procured from the commercial market based on the size and requirement according to specific reactors. The arrangement of packing materials in the packed bed reactors can be continuous or in multiple stages. Packed bed reactors can be used for removal of nitrate in denitrification process and also in anaerobic treatment for highly concentrated industrial wastewater. Higher volumetric loading is possible in packed bed reactor. Biodegradation of chlorophenol and fluorine polycyclic aromatic hydrocarbon in packed bed bioreactor system has been reported in the literature by using mixed bacterial consortium and LDPE immobilized *Pseudomonas pseudoalcaligenes*, respectively (Zilouei et al. 2006; Sonwani et al. 2019). Pictorial representation of packed bed reactor is given in Fig. 11.3.

11.6.1.4 Membrane Bioreactor

Membrane bioreactors are basically developed after the ultrafiltration, nanofiltration, microfiltration, and reverse osmosis. In membrane bioreactor, the soluble enzyme and substrate are introduced on one side of the membrane, and from the other side, the product is forced out through the membrane (Fig. 11.4). It is operated with microorganism agglomerated in the form of flocs and preserved in suspension by stirring. The membrane acts as a selective barrier to these flocs. This bioreactor

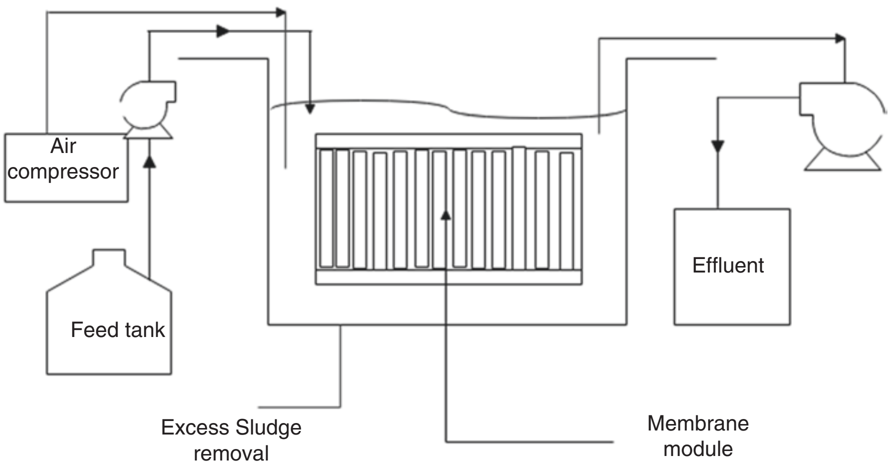


Fig. 11.4 Schematic diagram of membrane bioreactor

permits the separation of flocs (sludge) from the aqueous phase to relative phase. Recently developed submerged membrane bioreactor shows the reduction of energy consumption. In this, hollow fiber membrane module is submerged in the bioreactor system operated in different environmental conditions, i.e., anaerobic, anoxic, and aerobic. Ammonia and phenol up to 1000 mg/L can be removed by using aerobic submerged membrane bioreactor as reported by (Rezakazemi et al. 2018).

11.7 Factors Affecting Biodegradation

11.7.1 Temperature

Temperature is one of the important environmental factors, which can alter the biodegradation ability of the microbes. Different types of microbes can survive in wide range of temperature. The temperature can alter the kinetics. Hence the optimization of temperature is quite essential for conducting biodegradation process. The temperature dependency of reaction rate constant can be estimated by Van't Hoff-Arrhenius relationship (Metcalf and Eddy 2014). The increasing in the temp increases the rate of biodegradation. Most of the fungus and algae are well grow in lower temperature. PAH compounds can be easily biodegraded at high thermophilic range (55 °C). Manzano et al. (1999) have reported about the biodegradation of nonylphenolpolyethoxylate where the growth rate increases with increase in temperature (i.e., 8.936 at 25 °C). Bacterial growth rate is double for each 10 °C hike. At higher temperature the degradation of aromatic compound was more due to the higher metabolic activity and higher bacterial density. Bauer and Capone (1985) reported that the temperature and oxygen content are two important rate-limiting factors for mineralization of PAH compounds. Armenante et al. (1999) discussed about the effect of temperature on the degradation of halogenated phenolic compounds. The rate of dehalogenation increased with increasing in temperature from 25 to 30 °C. The high phenol degradation has been reported by using *P. putida* at 30°C. Here, the rate of degradation increases with increase in temperature (El-Naas et al. 2009).

11.7.2 pH

pH plays a vital role for biodegradation as well as biodeterioration. Lower pH is excellent for the microbial attack. The pH range for the biological growth is 6.5–7.8. The pH of the medium gradually drops down when the growth of the microbes is good. The higher pH inhibits the algal growth (Falkiewicz-Dulik et al. 2015). From the earlier reported literature, PAH compound (phenanthrene) easily degraded at acidic pH (6.5) using *M. vanbaalenii* PYR-1 (Kim et al. 2005). Similarly, Dursun and Tepe (2005) reported that phenol removal and microbial (*Ralstonia eutropha*) growth rate is high at pH 7, but it decreases at acidic and alkaline pH.

11.7.3 C/N Ratio

Microbes require nutrient for their cell growth and replication. If the carbon source is more or less, it affects the overall growth of microbes. Carbon source is an important factor for nitrification/denitrification reaction. The nitrification efficiency and dynamic behavior of nitrifiers and heterotrophs are greatly affected by C/N ratio (Wang et al. 2009). At high C/N ratio, the growth rate of the heterotrophs is more than the nitrifiers (Xia et al. 2008). Hence, the nitrification process is getting retarded in the biodegradation process.

11.7.4 F/M Ratio

Food/microbes ratio is one of the important factors to investigate about the efficacy of the wastewater treatment system. F/M ratio can be adjusted by changing recirculation ratio. Lesser F/M ratio prevents induction of enzymes, and higher F/M ratio is toxic for the microbes, hence increasing the lag phase. The food is considered as COD and BOD loading to the treatment system and microbes present in the existing system. F/M ratio of 0.75 is adequate for biodegradation of phenol in anaerobic condition (Hussain et al. 2009). F/M ratio can also affect the sludge granule size which is important for the aerobic process. High F/M ratio makes faster and bigger size granules (Li et al. 2011).

11.8 Types of Bioprocess

11.8.1 Suspended Growth Process

In this process the microbes used to treat the wastewater are in the form of suspension and by means of mechanical mixing or aeration. The mixed liquor suspended sludge coming from the reactor to the clarifier contains high amount of active microbes which is subjected to recycle to the reactor as seed sludge. The activated sludge process is an example of the suspended growth process which is generally used for the municipal wastewater treatment process. In the suspended growth process, maximum percentage of solids can be separated by gravity settling. In aerobic system the heterotrophic bacteria produce polymeric material in the form of flocks which is continuously circulated through the reactor and comes in contact with the oxidizing organic pollutant. The main objectives of the activated sludge process are to remove the maximum possible oxidizable material and produce biological flocks. These two important factors should be considered at the time of optimization of aerobic suspended growth process. Multiple pollutants such as phenol, cresol, xylenol, quinoline, indole, and cyanide coming in coke oven wastewater are efficiently treated using aerobic suspended growth process (Sharma et al. 2018). Degradation of phenanthrene is also reported using mixed microbial culture under aerobic condition (Yuan et al. 2000).

11.8.2 Attached Growth Process

In this process the microbes are attached to a support medium, and the support medium can be a fixed one or a moving one. The microorganisms degrade the organic material and form a biofilm through which it is attached to the support material. The excess growth of biomass is sloughed from the carrier material and allowed for disposal. Tricking filter, rotating biological contactor, and fluidized bed reactor are the examples of attached growth process. In the past few years, the attached growth process is considered to be the most promising treatment system in the field of environmental engineering. Passive aerated biological filter is one of the emerging treatment systems for the high organic loading wastewater which helps to reduce the energy cost of treatment process (Ismali and Twafik 2016; Abou-Elela et al. 2019). Different types of carrier materials such as jute fiber, plastic fiber, and polyester fiber are effectively used as carrier materials for successfully treating the slaughter house and other wastewaters (Aziz et al. 2018; Rodriguez et al. 2011).

11.9 Modified Bioremediation Techniques for Heterogeneous Compounds

11.9.1 Sequential Bioreactor (SBR) System

Sequential bioreactor system has drawn the attention of many researchers due to its innovative applications in the wastewater treatment. In this treatment more than one reactor is connected series. Sequential bioreactors work on different modes such as filling, mixing, reacting, sedimenting, and decanting. These reactors can be used in various biochemical environments like organic removal followed by nitrification and denitrification. This type of reactors mainly used for removal of toxic organics as well as nitrogen and other inorganic pollutants. Based on the characteristic of the wastewater hydraulic retention time, organic loading rate and sludge retention time can be changed in sequential bioreactor system. Nowadays researchers pay more attention to hybrid treatment systems for wastewater management. Combinations of attached and suspended growth systems are together used in SBR to handle high organic loading (textile industry effluent) and shock loading problems (Shoukat et al. 2019).

11.9.2 Anammox Process

It is also one of the innovative biological treatment processes to treat the ammonia-nitrogen-rich wastewater. In this process, ammonium ion is oxidized into nitrogen gas under anaerobic condition where autotrophic bacteria oxidized and converted inorganic carbon to cellular carbon using nitrite as electron acceptor (Rittmann and McCarty 2012). Anammox process has been used to treat landfill leachate, coke oven wastewater, and pharmaceutical wastewater (Liang et al. 2009; Toh and Ashbolt 2002; Tang et al. 2011). The first full-scale anammox treatment plant was established and operated in the Netherlands (Jin et al. 2012). Anammox bacteria possess slow growth rate and less yield and are very much sensitive to other environment conditions. Hence, it is difficult to grow the anammox bacteria and maintain suitable environment for this process which is the main drawback of this process. Excess amount of ammonium-nitrogen also shows the inhibitory impact to the anammox bacteria. The release of free ammonia from the anammox process leads to reduce the process efficiency. Synergistic effect of anammox bacterial with denitrifying bacteria is also mentioned in literature. But it is difficult to maintain the dissolved oxygen and pH in a single reactor. Therefore to overcome these issues, the pH of this process should be always maintained at neutral condition. Some additional pretreatment techniques must be adopted to treat the inhibitory compounds present along with other pollutants. Anammox sludge should be intermittently added to maintain the good quantity of anammox bacteria within the reactor. Dissolved oxygen is also a key factor for anammox process; therefore air saturation level should be maintained between 2% and 18% (Jin et al. 2012).

11.9.3 SHARON Process

SHARON (single reactor system for high ammonium removal over nitrite) process is used to treat high-nitrogen-comprising wastewater. This process takes place at high temperature (35 °C) using intermittently aerated CSTB with less retention time. Both AOB (ammonia oxidizing bacteria) and NOB (Nitrite oxidizing bacteria) are essential to operate this system. NOB is commonly washed out due to less retention time and therefore nitrite only formed in SHARON reactor that reduces the pH. This process needs only less than 25% of oxygen and 40% of carbon source to convert the nitrite from ammonia than nitrate (Van Dongen et al. 2001). SHARON process coupled with anammox process is used to treat the landfill leachate and refinery wastewater which contain high amount of nitrogen with cyanide, phenol, and sulfide (Shalini and Joseph 2018; Milia et al. 2012). Here, SHARON process used followed by anammox process.

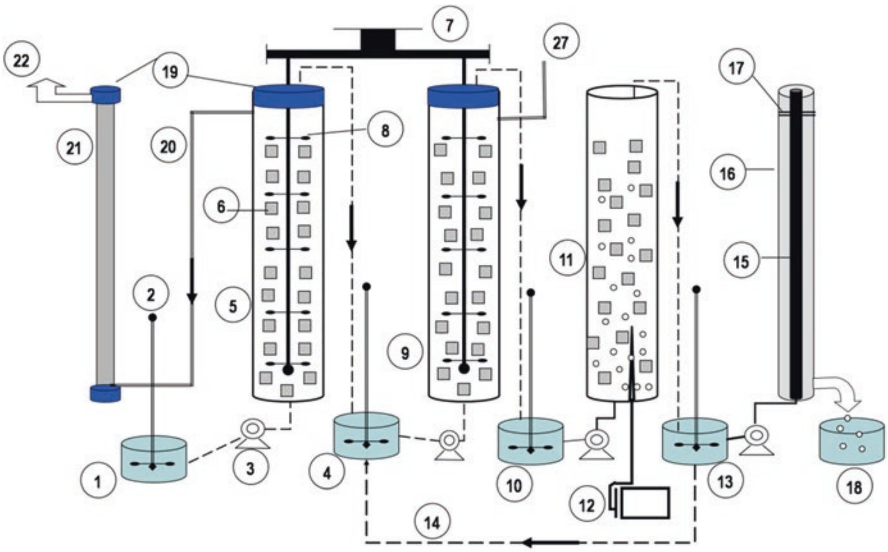
11.9.4 Moving Bed Bioreactor (MBBR)

MBBR technology developed from the activated sludge process and bio filter process. In MBBR different types of carrier material were used over which the biomass can grow. MBBR is connected in series to establish the sequential MBBR to achieve the continuous contact of biomass with pollutants. Selection of biomass carrier material in MBBR is one of the key factors which enhance the growth of biomass with higher surface area (e.g., polyurethane foam, polyethylene media, etc.). MBBR can also be operated in different environments (i.e., anaerobic, aerobic, and anoxic). Biomass in MBBR can be in suspended or attached form. This process has many advantages such as no sludge bulking issues, less sludge production, and resistance to higher organic loading and shows very good removal efficiency. MBBR is successfully used for treatment of slaughter house and refinery wastewater. Coke oven wastewater containing a variety of pollutants and phenolic wastewater can also be efficiently treated by MBBR (Sahariah et al. 2016; Borghai and Hosseini 2004). It can be used as potential treatment technique with high sludge retaining time.

11.9.5 Modern Hybrid Systems

Combination of two or more treatments combined in a single system to achieve the zero pollutant discharge is called as hybrid treatment system. For instance, (a) suspended cum attached growth process and (b) sequential bioreactor combined with physicochemical reactor are some of the familiar hybrid systems. Use of the biological process in real field at higher scale is a big challenge for the environmental engineers due to the persistence nature. Recently researchers have developed many novel hybrid techniques to handle the multi-toxic compounds. In this context three-stage anaerobic-anoxic-aerobic and four-stage anaerobic-anoxic-oxic-oxic bioreactors have been developed and successfully used for treatment of refractory chemical and PAH compounds present in coke oven wastewater (Zhou et al. 2017, 2018). Novel integrated hybrid treatment approach is also an advanced treatment strategy in the field of environmental engineering. Recently, Ren et al. (2019) have reported that integrated hybrid process can be used as efficient technique to treat the PAHs, phenols, BTEXs, and heterocyclic compounds coming from coking wastewater reclamation plant. In this study, anaerobic-aerobic-coagulation-sand filter-ultrafiltration- adsorption-nanofiltration-RO system has been proposed to target each pollutant for efficient removal in a specific unit according to its characteristics.

The addition of gas absorption unit in the hybrid process can be another value addition to the integrated hybrid treatment system. Recently, a potential hybrid system has been developed in the field of biological wastewater treatment which is known as integrated biophysical hybrid reactor system (Anandkumar 2016). It is a combination of sequential physical and biological process. The integrated biophysical hybrid reactor system is established for the remediation of high loading of organic and inorganic pollutants or heterogeneous pollutants resulting from various processes of industries. This hybrid reactor comprises of three units, namely, anaerobic-anoxic-aerobic sequential bioreactor, gas absorption unit, and polishing



1. Feed tank, 2. Stirrer, 3. Peristaltic pump, 4. Anaerobic reactor, 5. Anaerobic effluent, 6. Sponge cube, 7. Mechanical stirrer, 8. Baffle, 9. Anoxic reactor, 10. Anoxic effluent, 11. Aerobic reactor, 12. Aerator, 13. Aerobic effluent, 14. Recycle, 15. Cationic packed bed column, 16. Anionic packed bed column, 17. Connector of cationic and anionic column, 18. Final effluent outlet, 19. Air tight cover, 20. Gas collecting tube, 21. Gas adsorption column and 22. Exit gas tube

Fig. 11.5 Schematic diagram of biophysical hybrid reactor system unit. The integrated biophysical hybrid reactor system is shown in Fig. 11.5. In the first step, a three-stage anaerobic-anoxic-aerobic sequential bioreactor system is used wherein each reactor consists of three equal sections packed with sponge cubes as biomass carrier to obtain the maximum pollutant removal efficiency. Secondly, in gas absorption unit low-cost and recyclable adsorbent is used for the removal of various gaseous by-products coming from the anaerobic and anoxic units. In the third stage, surface-modified coal fly ash-based cationic and anionic ceramic adsorbents are packed in the inbuilt cationic-anionic polishing unit to achieve the zero pollutant discharge in the effluent after treatment.

11.10 Conclusion and Future Scope

This chapter describes the different types of heterogeneous pollutants coming from industrial effluents and their toxic effects. Various physicochemical treatment techniques exist to handle these pollutants, and their merits and demerits are discussed. Also, it comprises different biological treatment processes applied for treatment of pollutants coming from different industries. Different types of bioreactors as well as newly modified processes and the factors affecting the biodegradation process are included. Biological treatment processes have many advantages as well as some limitation. Considering these limitations of bioprocess therefore users can modify the process according to the necessity. Some researchers have recently developed new hybrid bioreactor systems with certain modifications to handle the heterogeneous pollutants to attain the zero pollutant discharge in the effluent which shows the realistic approach of the biological wastewater treatment system. In future, there will be a great demand for eco-friendly hybrid systems in clean technologies to deal the global water pollution challenges.

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